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Title: Neutron Reflectometry for the Study of Thin-Film Ionomers

Author(s): Richard, Derek Michael

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Neutron Reflectometry for the Study of Thin-Film Ionomers

Effect of Substrate and Cation Exchange on Ionomer Structure

Derek Richard
Los Alamos National Lab

FUEL CELL PERFORMANCE AND DURABILITY

Personal Background

<u>A little about me:</u>

- **Attended the University of Arkansas for bachelor in chemical engineering**
- **Internship at Cross Oil Refinery South Arkansas**
- **Research under Dr. Lauren Greenlee**
    - Reclamation of phosphorus from waste water by electrochemistry
    - Microelecrode, split and single cell.
- **WERC design competition**
    - Novel process for removal of gypsum from mine waste water
- **Los Alamos National Laboratory, Materials Physics and Applications group (MPA-11)**

LANL

Los Alamos National Lab

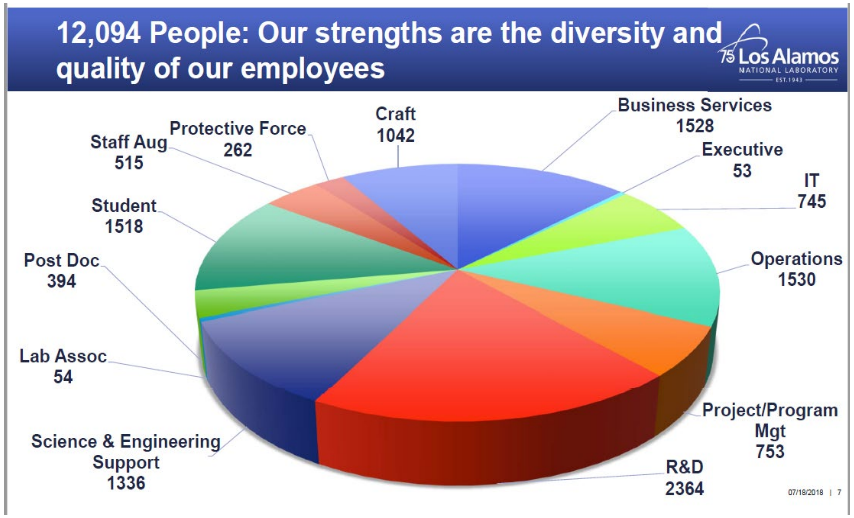
U.S. Department of Energy

36 square miles of DOE-owned property

More than 2,000 individual facilities, including 47 technical areas with 8 million square feet under roof including

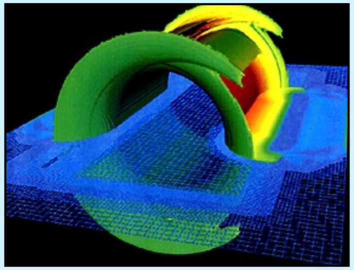
Los Alamos is located in the South-Western U.S., in the mountains in Northern New Mexico at 7500 ft. elevation (2300 meters)

Picture overlooking the main technical area of Los Alamos, from the Pajarito Ski Area



LANL Mission: National Security

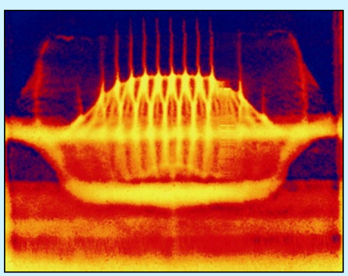
Stockpile Stewardship



Large-Scale Simulation

Stockpile Stewardship

B61-7/11 Strategic Bomb



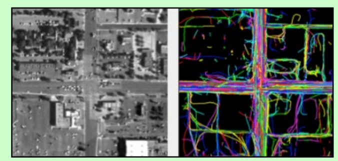
Proton radiography

Pit Manufacturing

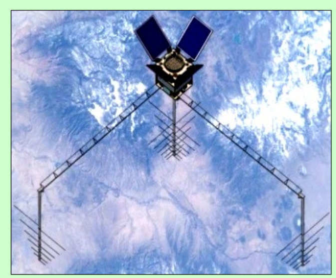
W76, W78, W88
for Trident &
Minuteman III

Global Security

Non Proliferation



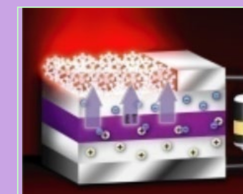
Intelligence Analysis



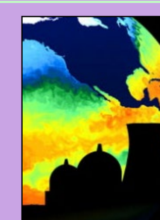
Space Systems

Six other product lines

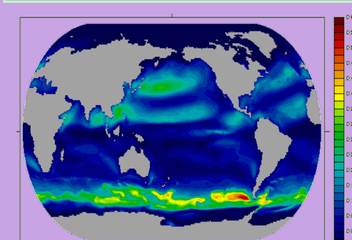
Energy Security



Materials and Concepts for Clean Energy

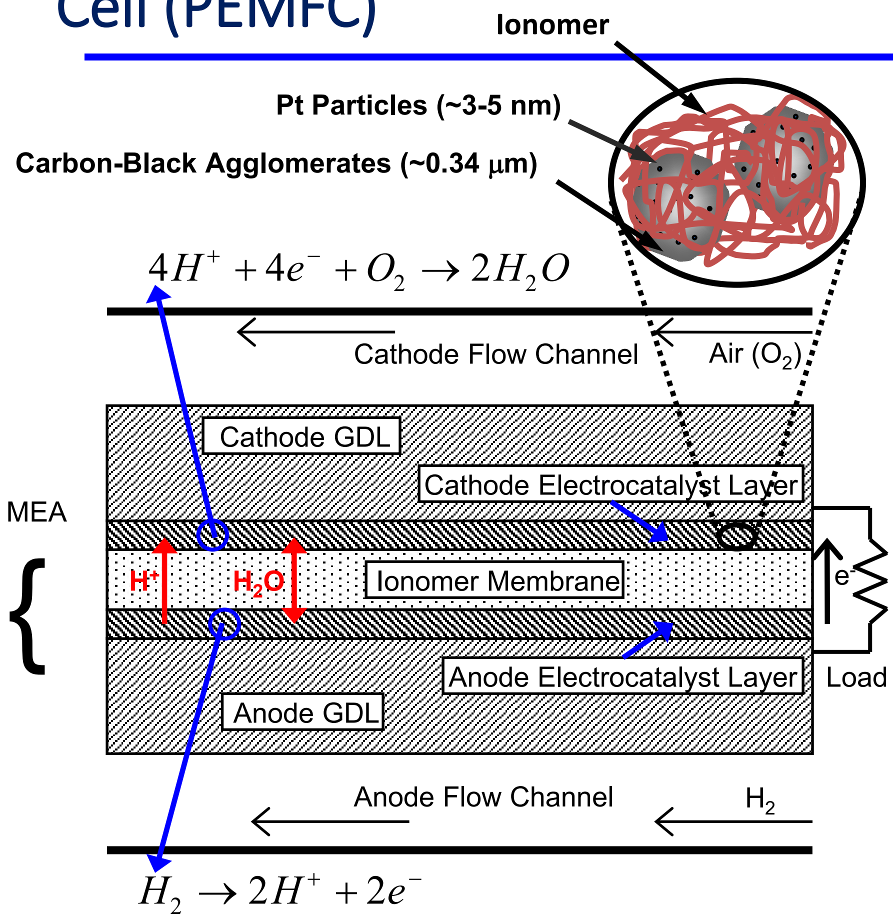


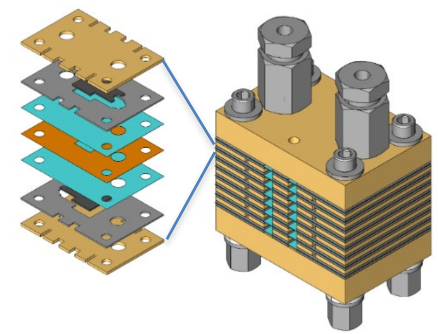
Nuclear Energy



Climate Energy Nexus

Components: Polymer Electrolyte Membrane Fuel Cell (PEMFC)





Membrane: Perflourosulfonic acid (10 – 25 micron)

Catalysts:
Anode: Pt, Pt-Ru
Cathode: Pt, PtCo, PtNi …

Catalyst Support: Carbons

Gas Diffusion Layer: Carbon fiber with micro-porous layer

Bipolar Plate: Carbon Composite, Coated Metal

FC-PAD: Consortium to Advance Fuel Cell Performance and Durability

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Fuel Cell Technologies Office (FCTO)

Approach	Objectives
Couple national lab capabilities with funding opportunity announcements (FOAs) for an influx of innovative ideas and research	• Improve component stability and durability • Improve cell performance with optimized transport • Develop new diagnostics, characterization tools, and models

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Consortium fosters sustained capabilities and collaborations

Core Consortium Team*

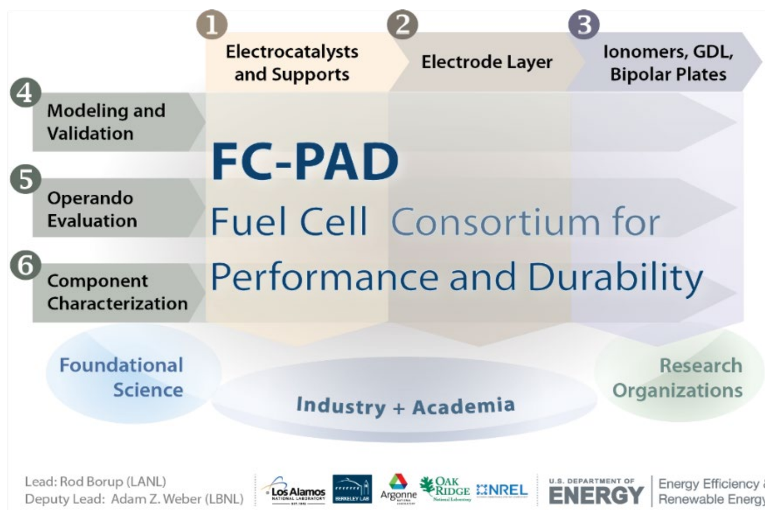
Argonne National Laboratory, Los Alamos National Laboratory, Berkeley Lab, NREL National Renewable Energy Laboratory, Oak Ridge National Laboratory

Prime partners added in 2016 by DOE solicitation (DE-FOA-0001412)

3M, GM, United Technologies Research Center, Vanderbilt

www.fcpad.org

Structured across six component and cross-cutting thrusts



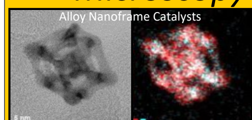
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

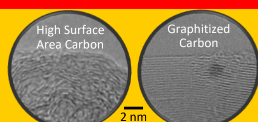
FC-PAD NL Capabilities

	Structural & Chemical Characterization		Performance Testing & Evaluation		Modeling & Theory
Catalyst & Catalyst Support	*Analytical Electron Microscopy*	*Advanced X-Ray Techniques*	*Electrode Fabrication*		*Electrode Simulations*
Electrode & MEA		*On-line Analysis of Catalyst Degradation*	*Advanced MEA Diagnostics*		
Membrane & Ionomer		*Advanced Component Diagnostics*	*Electrode Structure Evaluation*	*MEA Component Diagnostics*	*Multiphysics, Multiscale Models*
GDL & Cell	Transport property measurements	X-ray tomography	*MEA Fabrication*	*Performance & Durability Testing*	

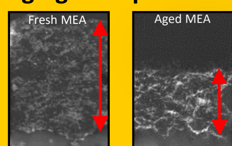
Structural & Chemical Characterization

Analytical Electron Microscopy

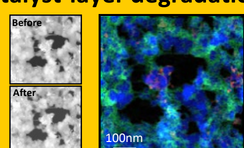




Imaging and spectroscopy



Catalyst-layer degradation

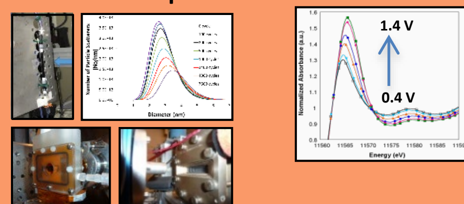


Ionomer mapping

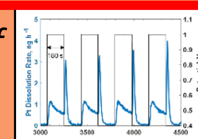
Oak Ridge National Laboratory MoreKL1@ornl.gov

Advanced X-Ray Techniques

Catalyst and support atomic structure and particle size



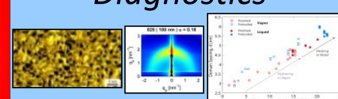
On-line Analysis of Catalyst Degradation



Pt and Co dissolution rate with potential

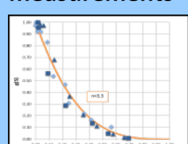
Argonne DMyers@anl.gov

Advanced Component Diagnostics

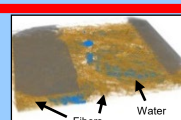


Bulk and thin-film morphology and properties

Transport property measurements



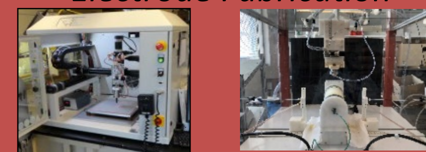
X-ray tomography



Berkeley Lab AZWeber@lbl.gov

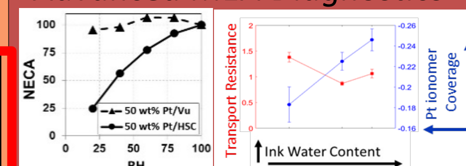
Performance Testing & Evaluation

Electrode Fabrication



Ultrasonic spray - electrospinning

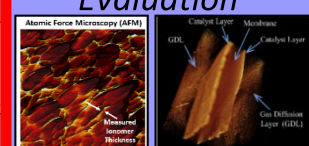
Advanced MEA Diagnostics



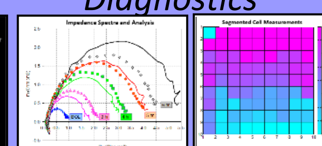
Transport - Accessibility - Coverage

NREL Kenneth.Neyerlin@nrel.gov

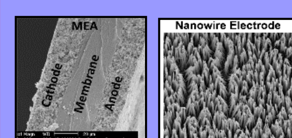
Electrode Structure Evaluation



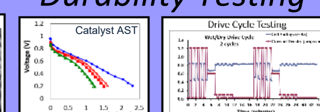
MEA Component Diagnostics



MEA Fabrication



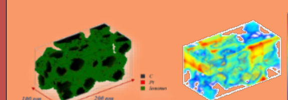
Performance & Durability Testing



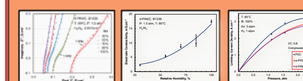
Los Alamos Borup@lanl.gov Mukundan@lanl.gov

Modeling & Theory

Electrode Simulations



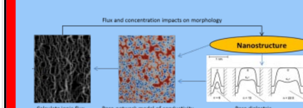
3-D electrode reconstruction and transport



Quantify various losses

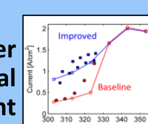
Argonne Walia@anl.gov

Multiphysics, Multiscale Models



Membrane simulations

Optimize water and thermal management



Berkeley Lab AZWeber@lbl.gov

Oak Ridge National Laboratory · Argonne · NREL · Los Alamos · Berkeley Lab

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Fuel Cell Testing

Test stations

- Used to measure the performance of operating fuel cells
- Fully controllable conditions (humidity, temperature, flow rates, pressures, load)
- Programmable run cycles and data collection (Break-in, pole curves, impedance, crossover, accelerated aging, etc.)

Fuel Cell Technologies Test Station

Bio-logic Potentiostat

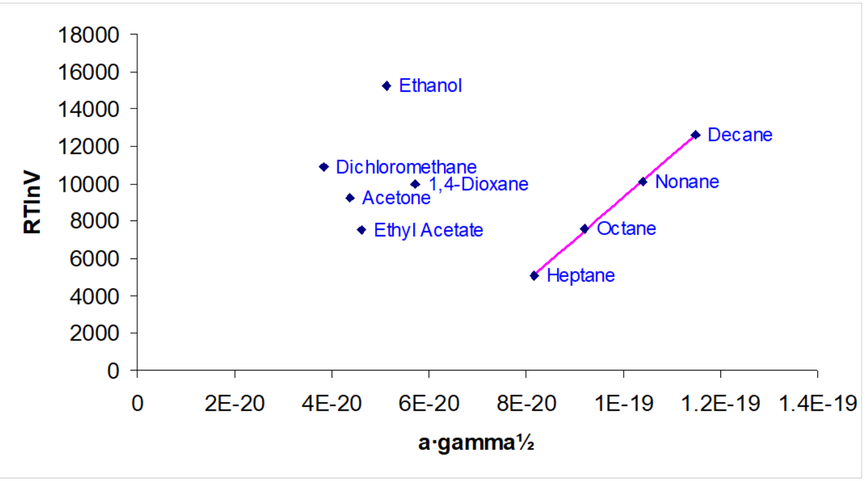
Potentiostat

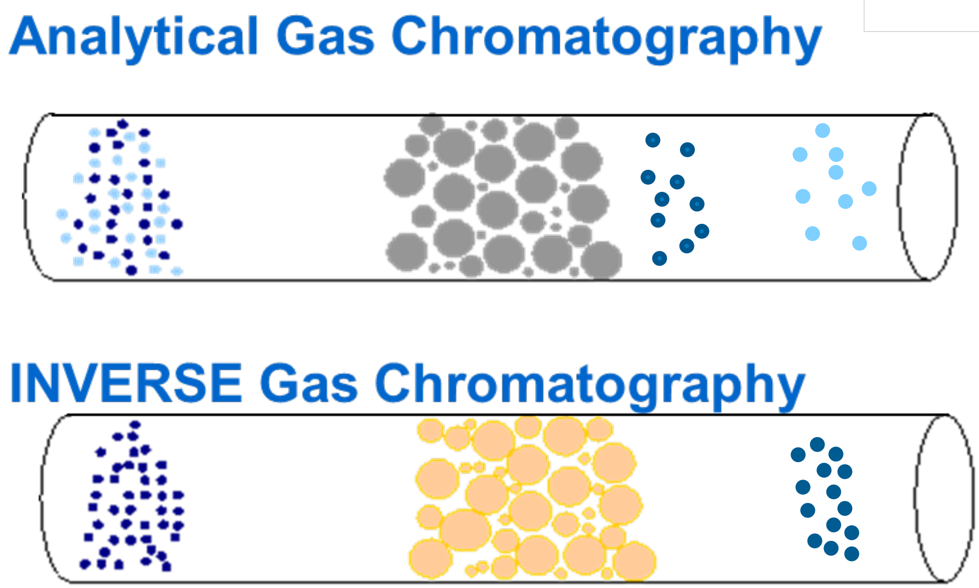
- Used in tandem with a test station to measure electrochemical performance of fuel cells
- Catalyst activity, accelerated aging, test for cross membrane shortages, etc.

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

IGC: Inverse Gas Chromatography

- Sample is stationary, probe is mobile
- Column packed with sample
- Gases of known properties are used to probe the sample



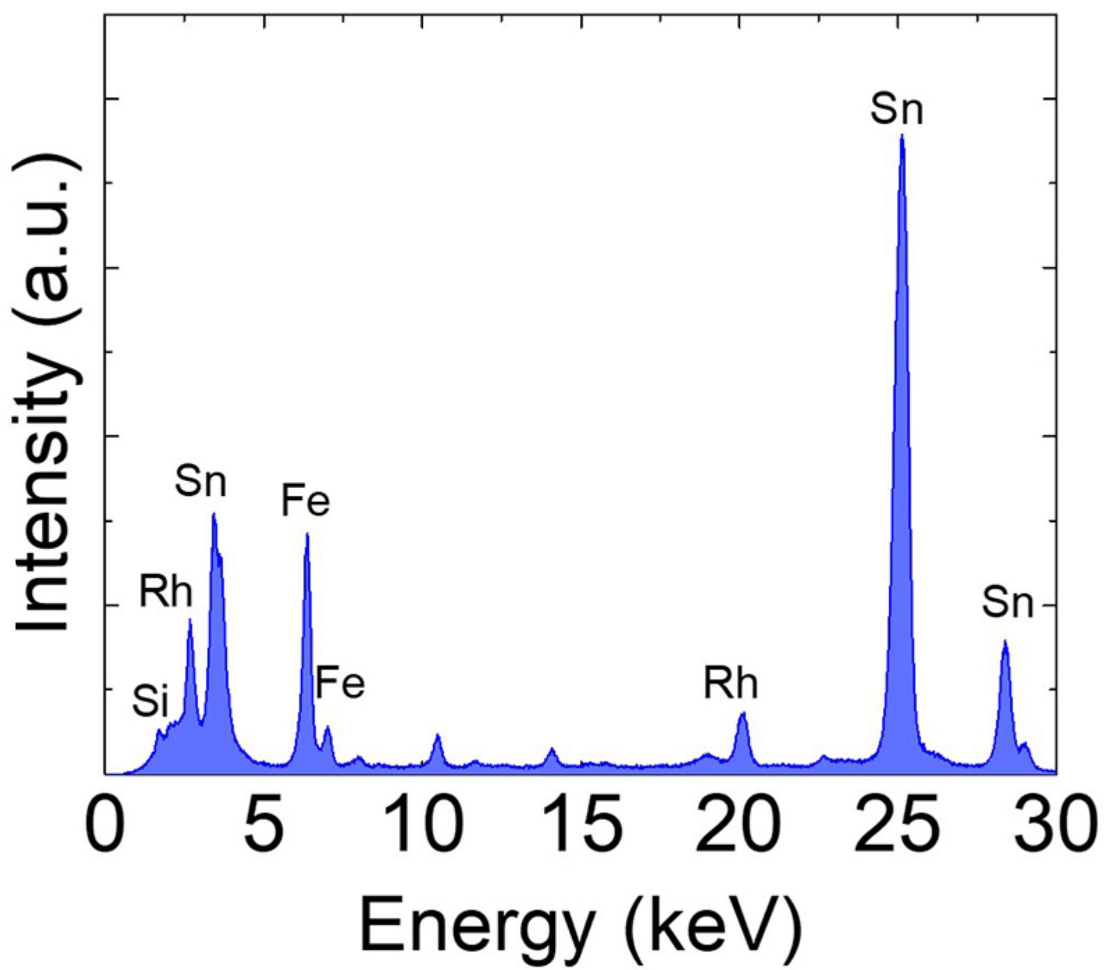


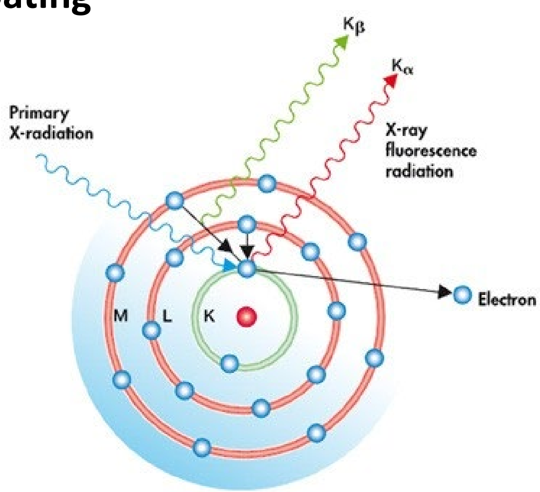
- Can measure various properties
- Primarily used for surface energy
- Surface wettability

XRF: X-Ray Fluorescence

- Uses X-Rays to determine presence of heavier elements
- Can determine concentration of compounds over a given sample area
- Typically used to measure Pt loading on Catalyst layers
- can also be used to determine thickness of thinfilm metals on Si wafers from sputter coating

http://imserc.northwestern.edu/services-pcm-xrf.html



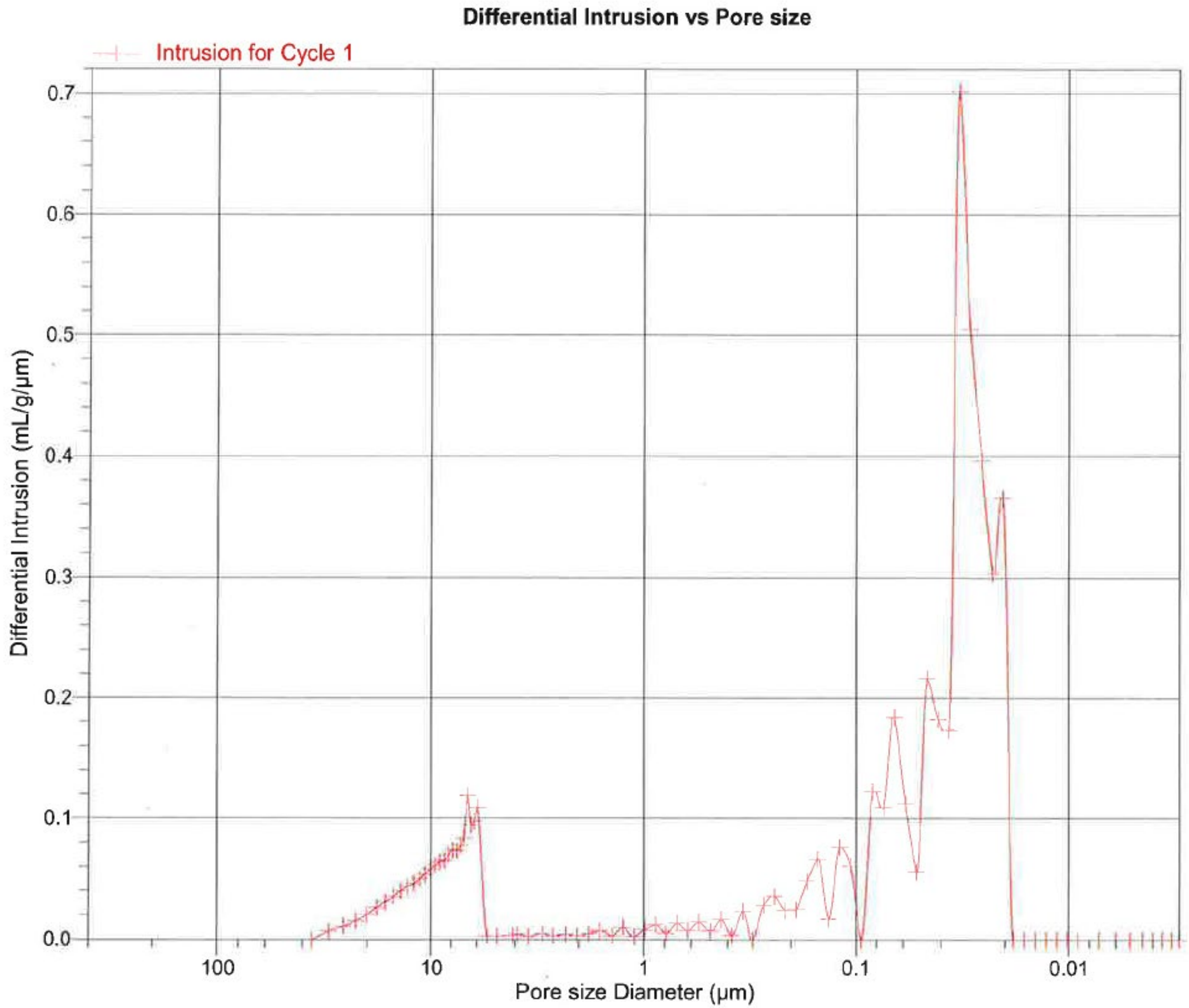


https://wpo-altertechnology.com/xrf-x-ray-fluorescence-spectroscopy-hi-rel-parts/

MIP: Mercury Intrusion Porosimetry

- **Measure mercury intrusion at increasing pressure to measure pore size and distribution**

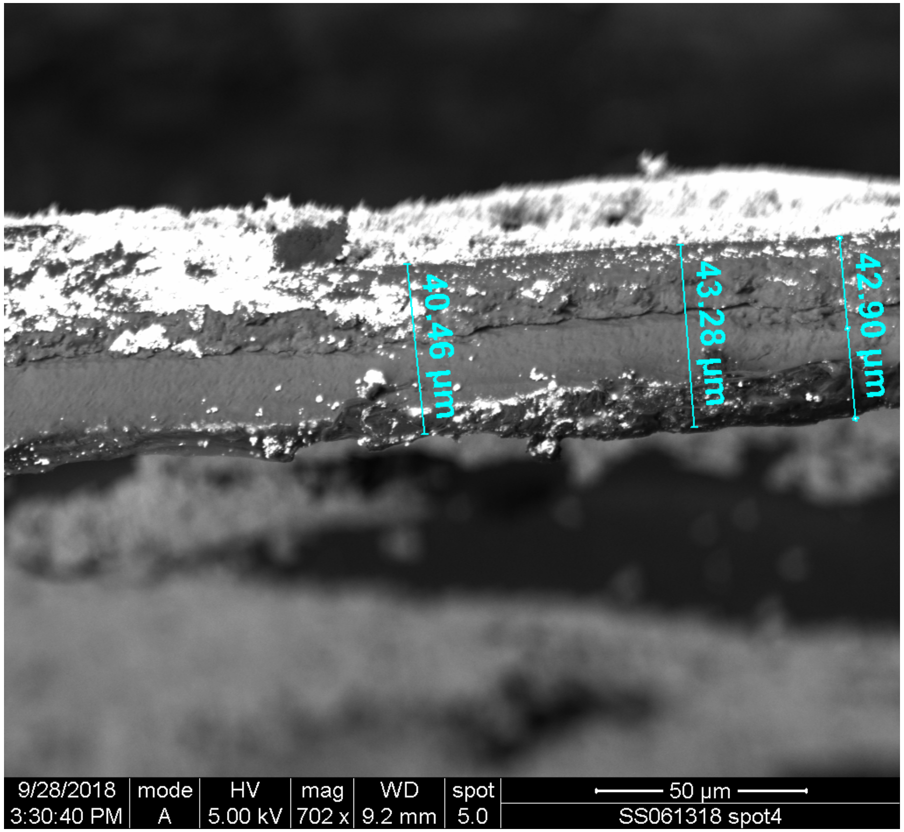
- **Useful for characterization of gas diffusion and catalyst layers**



FUEL CELL PERFORMANCE AND DURABILITY

SEM (Scanning Electron Microscopy)

- Micro scale imaging
- Cross sections of MEAS for determination of aging affects
- Elemental distribution (looking for contamination, catalyst distribution)
- Microscale- nanoscale morphology



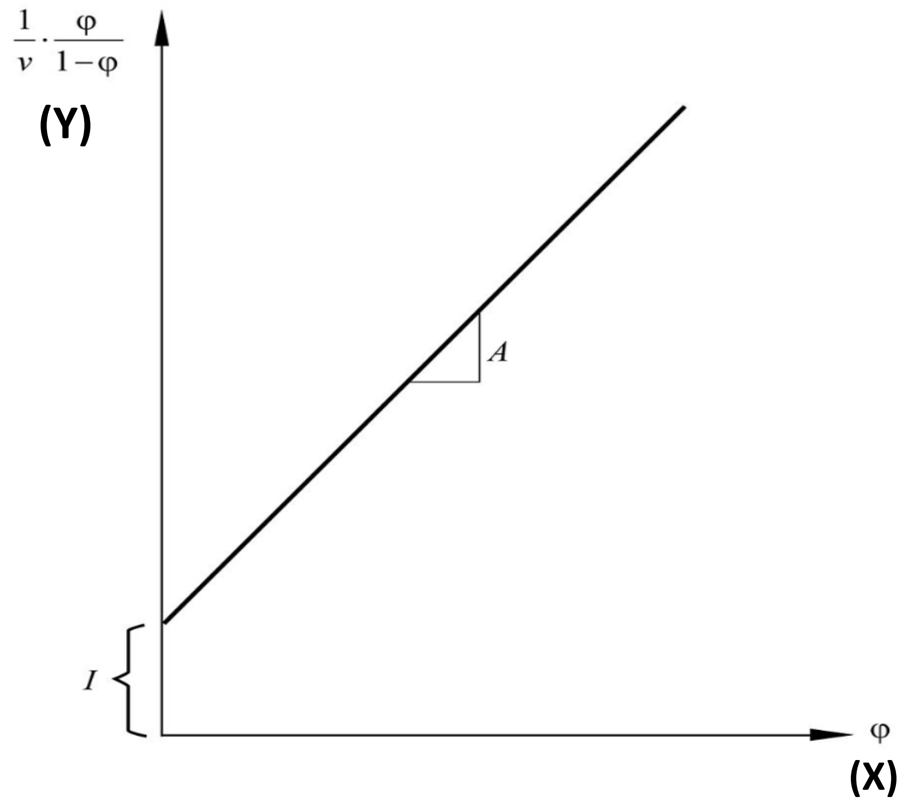
BET (Brunauer-Emmett-Teller) Surface Area

- Method for measuring specific surface area of solid surfaces
- Extension of Langmuir theory (monolayer molecular adsorption) to multilayer adsorption
- Gas diffusion layer, catalyst layer

$$\frac{1}{v\left[(p_0/p)-1\right]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c},$$

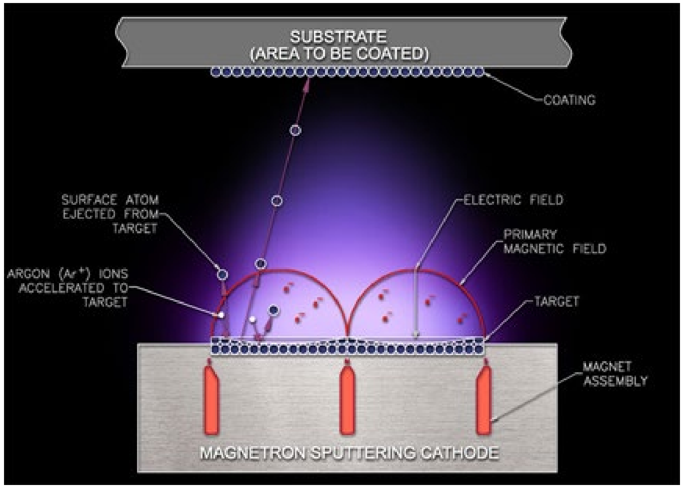
$$Y = A*(X) + I$$

Quantachrome Instruments autosorb iQ

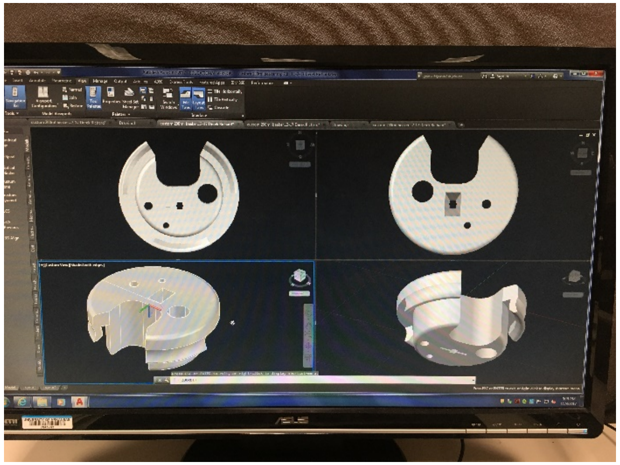


Other Techniques

- **Profilometry**
  - Laser and stylus
- **Spin Coating**
- **PVD (Physical Vapor Deposition) thin film sputter coating**
- **XRD (X-Ray Diffraction)**
- **XRR (X-Ray Reflectometry)**
- **3D modeling with AutoCAD and eMachineShop**



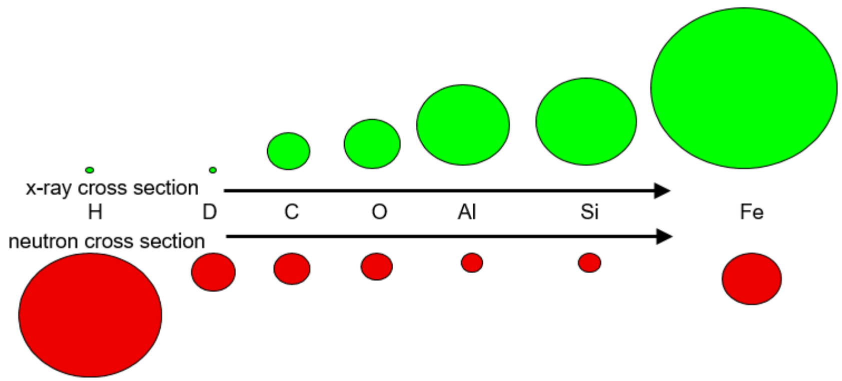
https://nptel.ac.in/courses/115103039/module16/lec39/4.html



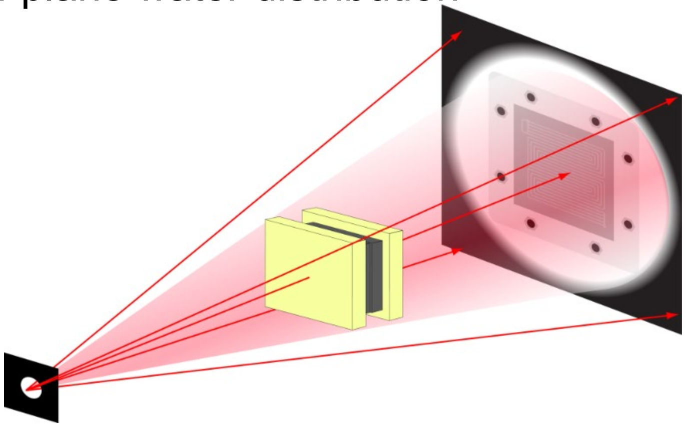
FUEL CELL PERFORMANCE AND DURABILITY

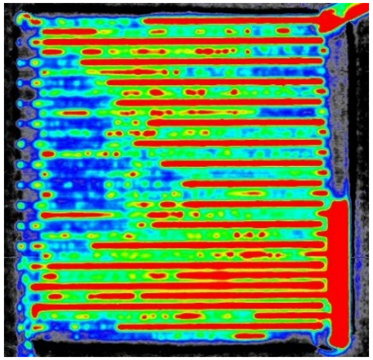
Neutron Imaging at NIST
Measuring Fuel Cell Water Management

Neutrons are an excellent probe for hydrogen in metal since metals have a much smaller cross section to thermal neutrons than hydrogen does.



In-plane water distribution



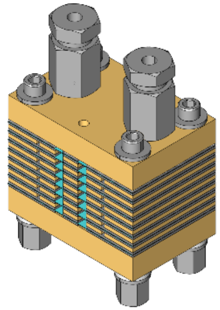


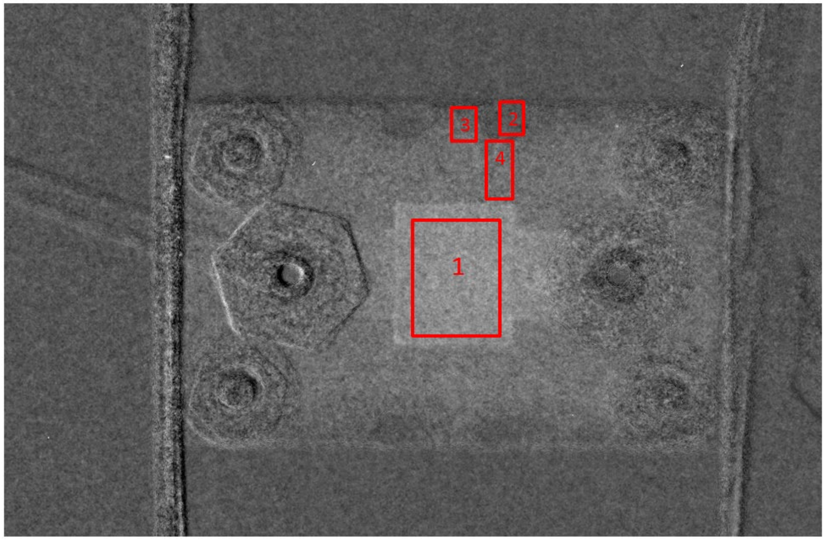
Beer-Lambert law

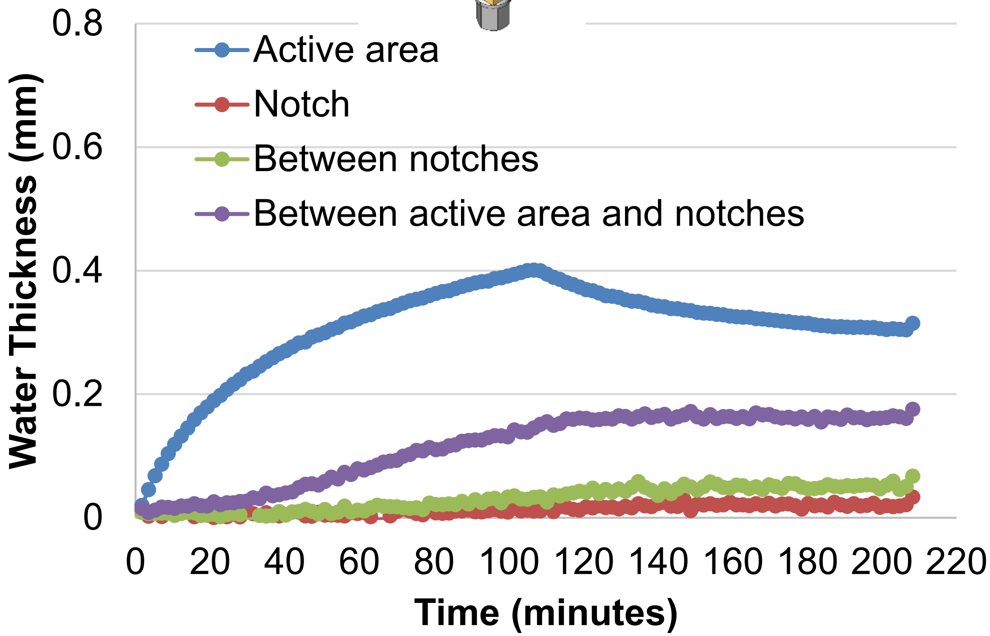
$$I = I_0 e^{-\mu t}$$

I_0 = reference (dry) image
I = attenuated (wet) image
μ = attenuation coefficient of water
t = liquid water thickness

Water content profiles 2b stack: 400 µm membrane stack (25C)







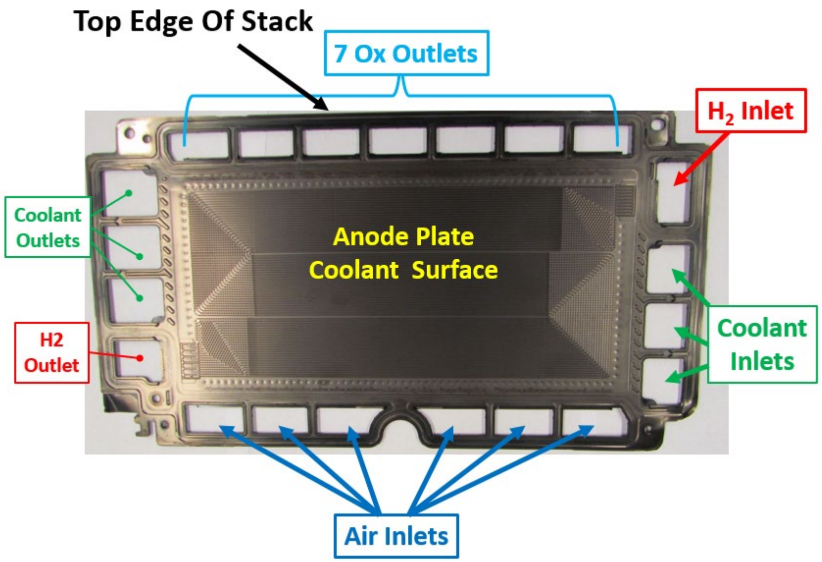
- wetting at 3 mA followed by subsequent natural dissipation.

- Monitoring water concentration during wetting/drying procedures
- Indicates water is removed (as designed) from active area by diffusion to exposed membrane at designed notches

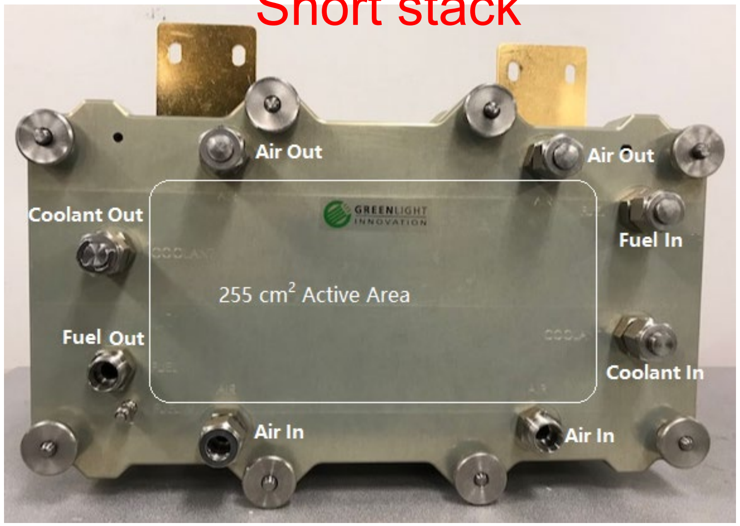
Commercial State-of-Art: Toyota Mirai

- 5 cell- 255 cm^2 active area per cell
- Stack from USCAR (Ford)
- Aged cells from USCAR (GM)

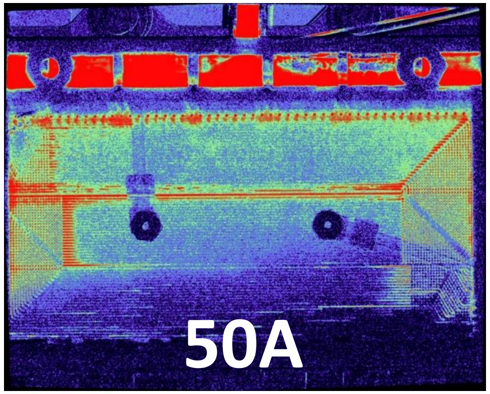
Mirai Cell



Short stack

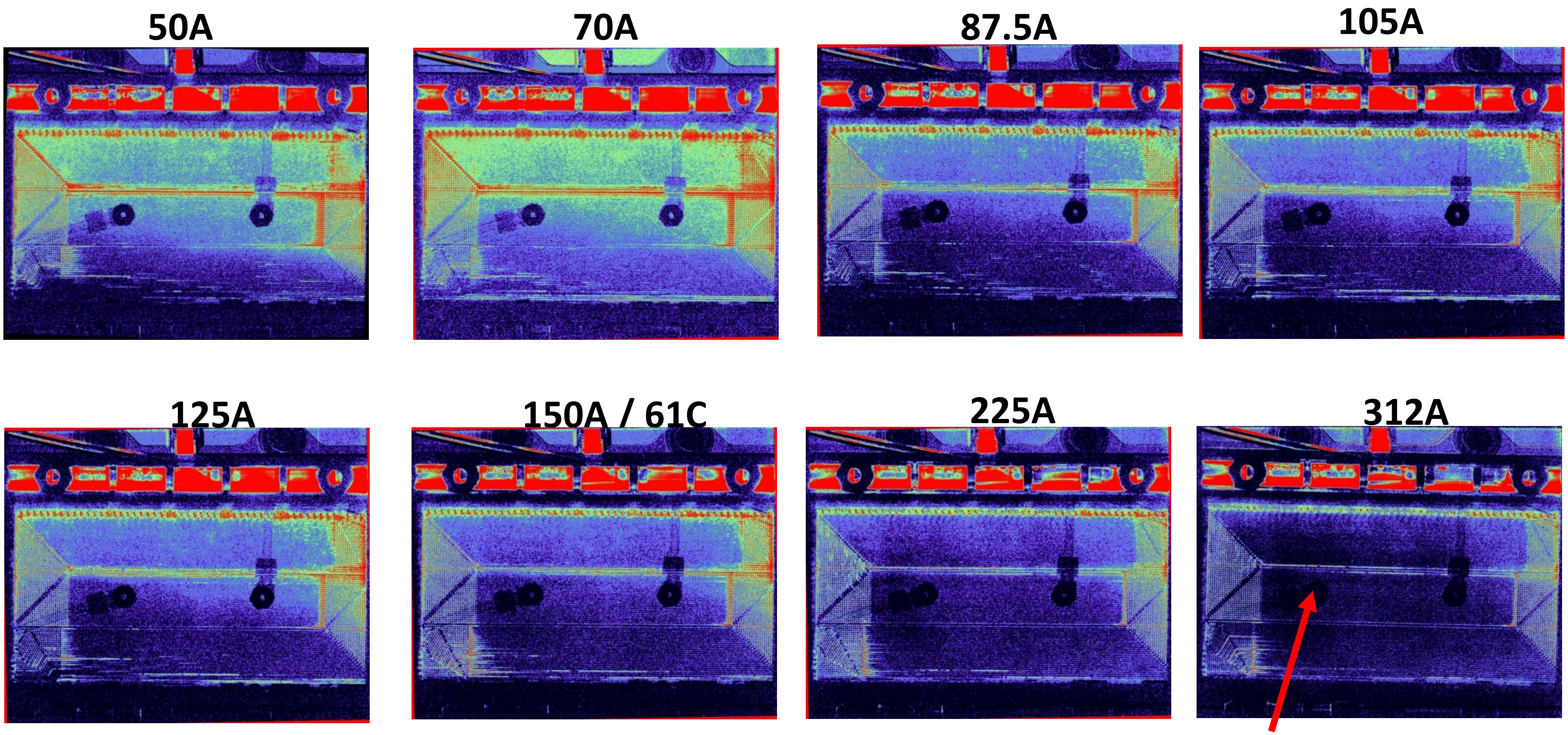


FC-PAD (LANL led Consortium) conducted full materials and performance analysis of Toyota Mirai fuel cell to set new benchmark for materials



Neutron Image (H_2O) of operating stack

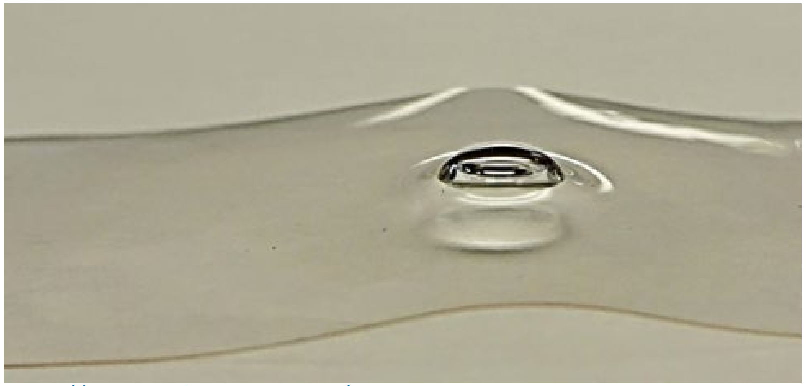
USCAR Matrix of Operating Conditions



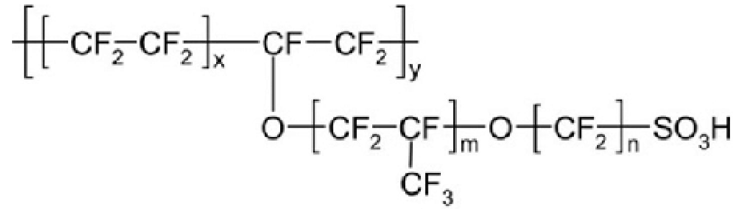
Notes: Unstable at *12.5 Amps*
450 Amp point insufficient H2

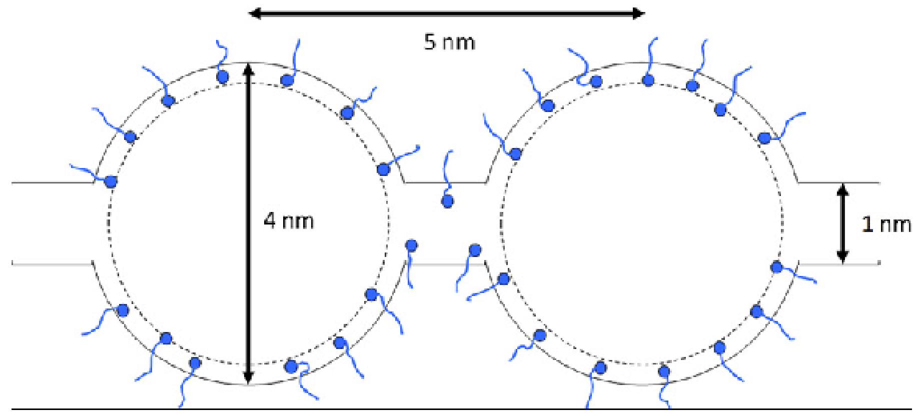
High Current & Flowrates show much less liquid water than low current/flowrates

What is Nafion: fuel cell electroyte



http://www.nafionstore.com/

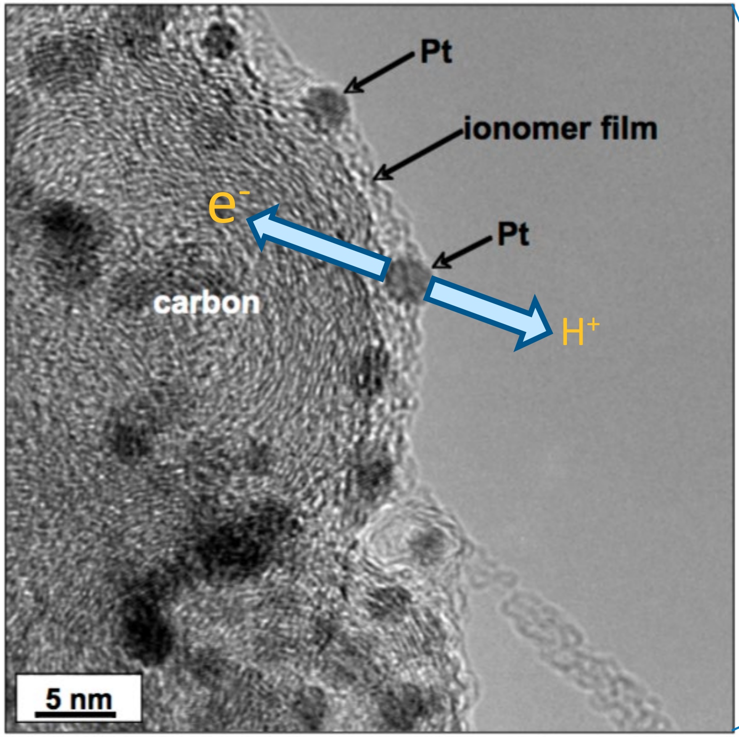




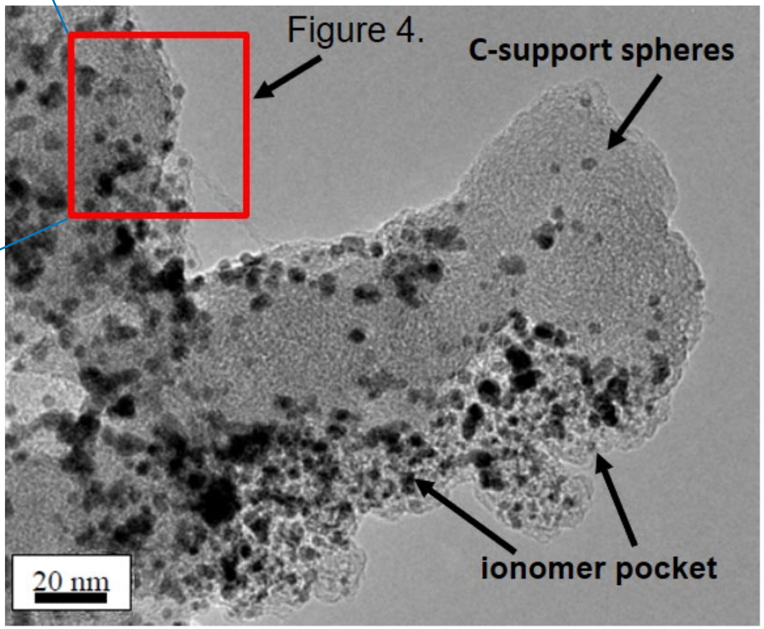
- Polyflourosulfonic Acid
- PTFE backbone (Hydrophobic)
- Sulfonic acid side chain (Hydrophilic)
- Creates water channels that conduct protons
- Does not conduct electrons
- Used as the electrolyte membrane and ionomer in PEM fuel cells
- Bulk behavior is well characterized
- Thin film regimes (ionomer) function differently and are not well characterized

Ye, Ruijie & Henkensmeier, Dirk & Yoon, Sang Jun & Huang, Zhifeng & Kim, Dong Kyu & Chang, Zhenjun & Kim, Sangwon & Chen, Ruiyong. (2017). Redox Flow Batteries for Energy Storage: A Technology Review. Journal of Electrochemical Energy Conversion and Storage. 15. 010801. 10.1115/1.4037248.

Why Look at Thin Film Ionomer?



- Thin ionomer layer coats carbon and Pt and is responsible for proton transport
- Affects mass transport properties (oxygen diffusion)



- Ce used as radical scavenger
- Co leaches from Pt/Co catalyst

Karren More, Rod Borup and Kimberly Reeves

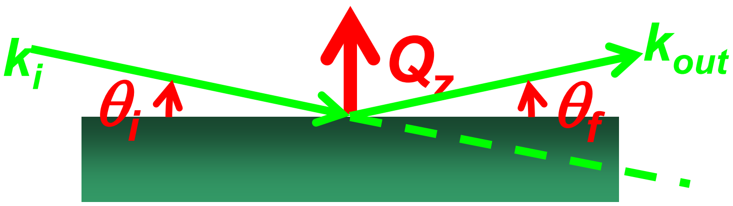
ECS Trans. 3(1), 717 (2006)

What is Neutron Reflectometry?

Technique used to investigate thin-film profiles for internal structure changes

<u>Advantages</u>

- Provides density, layering, roughness, and composition information
- Angstrom level resolution
- Effectively non-destructive
- Good resolution for low-Z elements
- Isotope sensitive (H vs. D)
- Neutrons are highly penetrative



$$k_{out} = k_i + Q_z$$

$$Q_z = 4\pi \sin\theta / \lambda$$

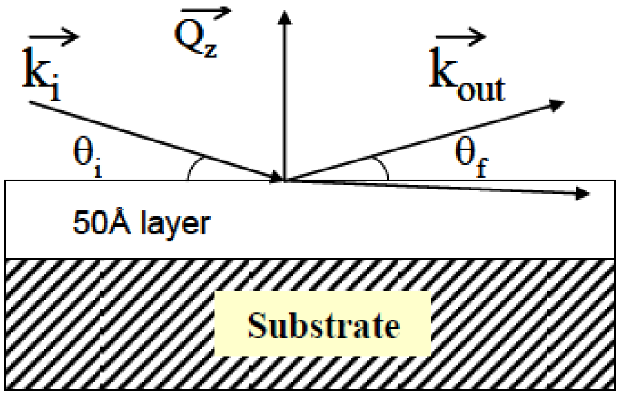
<u>Limitations</u>

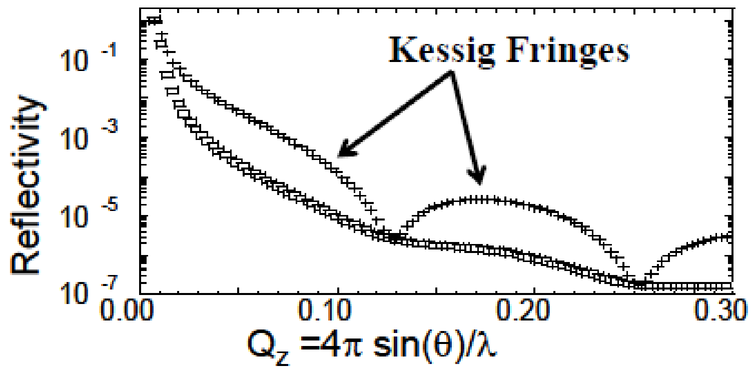
- Only provides information along vertical axis (z)
- Excessive layering can be difficult to conclusively model
- Needs large, atomically smooth surface

~4 locations in U.S.: LANSCE, SNS, NIST, HFIR

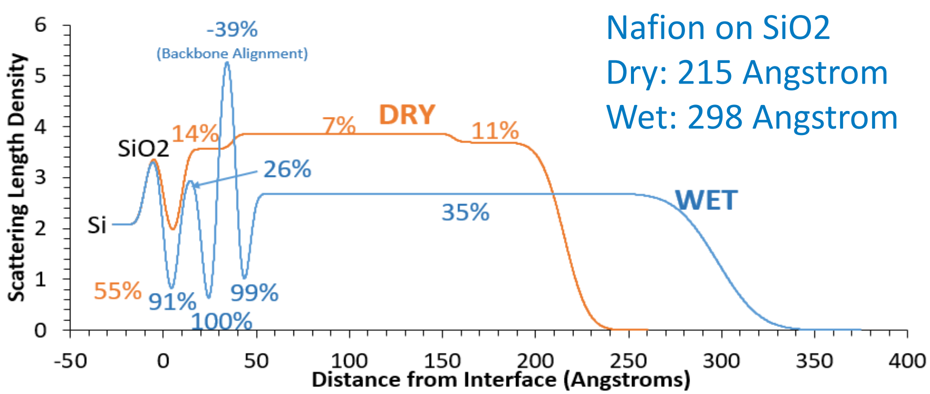
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

NR Basics





Schematic of single-layer NR experiment showing basic principles (left) and reflectivity profiles for a bare substrate and film/substrate system (right); reflectivity is dimensionless and Qz has units of Å-1.



Assuming dense Nafion SLD (Scattering Length Density) is 4.15 and knowing H2O SLD is -0.56

- Swelling
- H2O content

FUEL CELL PERFORMANCE AND DURABILITY

Sample Prep

Silicon wafer Substrate

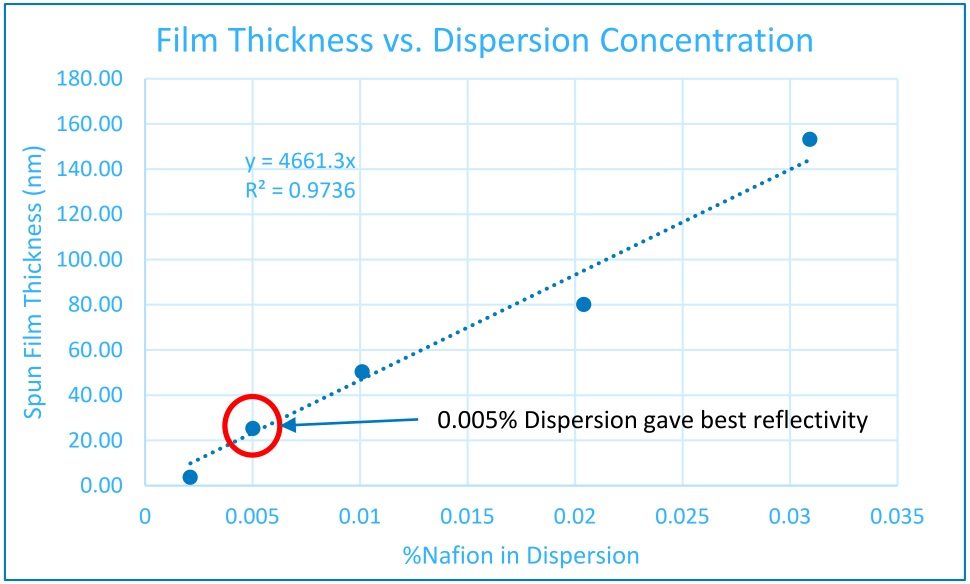
- UV-Ozone cleaned
- Native oxide layer
- Sputter coated platinum
- Sputter coated carbon

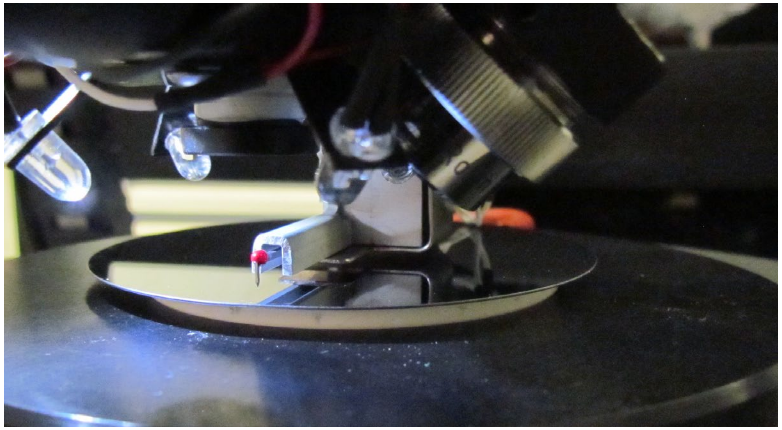
Coating Process

- Spin coated nafion/IPA Dispersion
- 3500 RPM 60 sec
- Annealed at 150C, 1hr

Doping Process

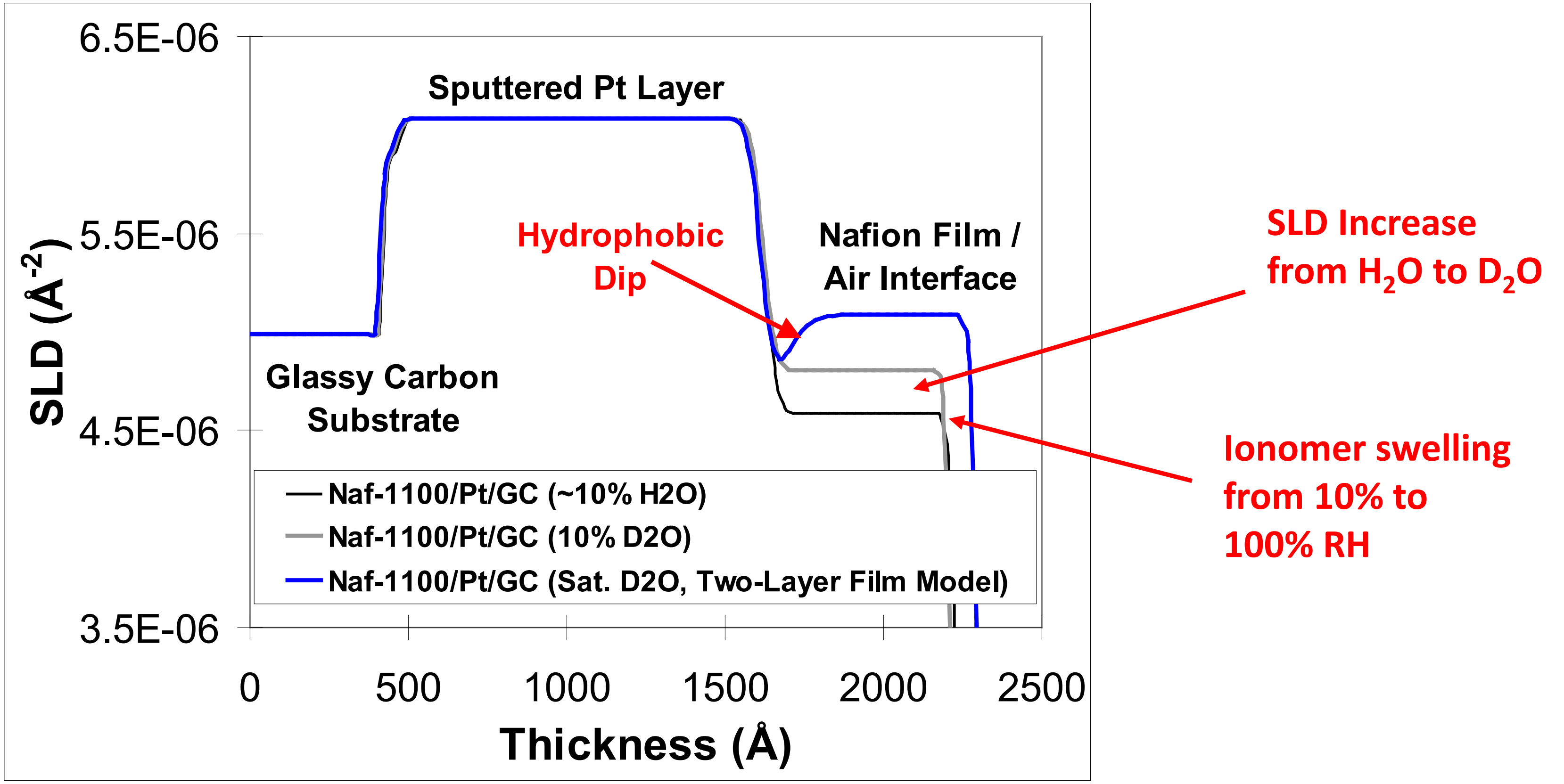
- Submersion in water with appropriate dopant
- Water bubble with appropriate dopant
- Dried at 50C
- Dependent on adhesion





Checking wafer surface roughness with profilometer

NR SLD profiles for Nafion® 1100/Pt bilayer system on GC substrate

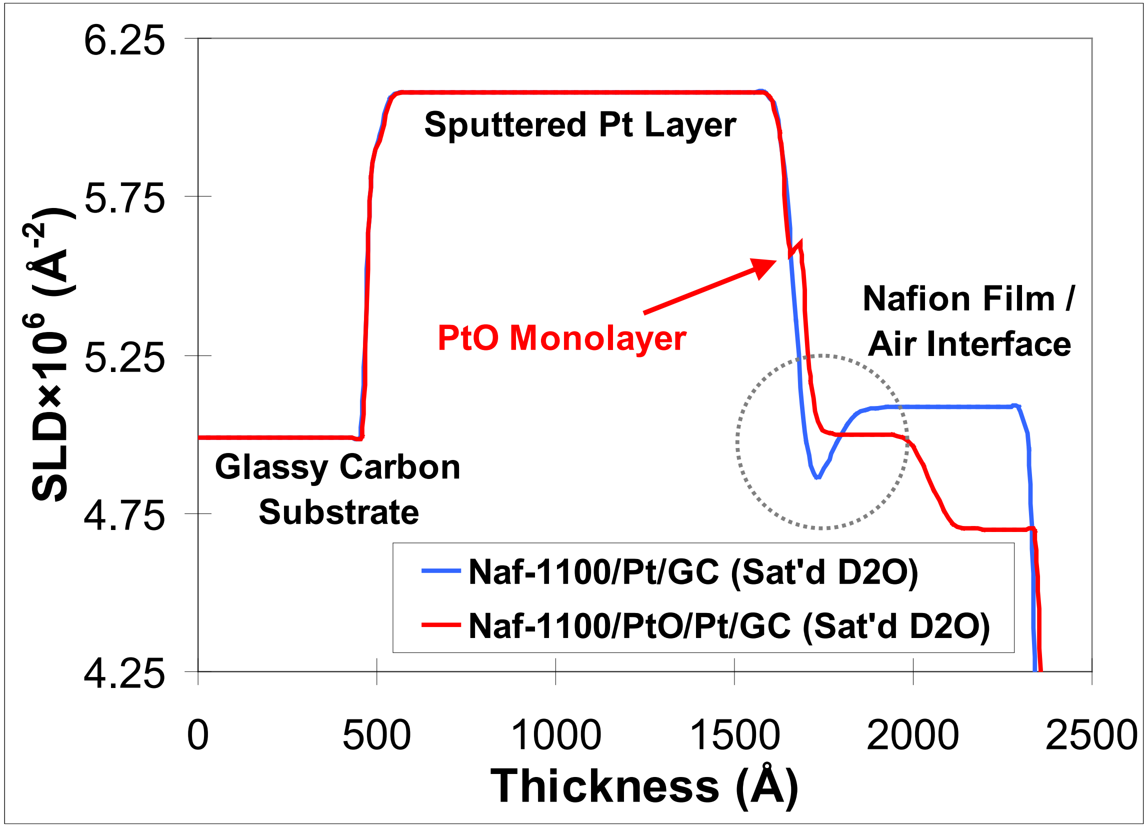


- Dip in SLD at Pt/Nafion interface for saturated D_2O indicates hydrophobic surface

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

D. L. Wood, J. Chlistunoff, J. Majewski, and R. L. Borup, J. Am. Chem. Soc. 131 (50), 18096-18104 (2009)

Nafion Structure comparison on Pt versus PtO



Nafion interface / water content rearranges with hydrophobic Pt versus hydrophillic Pt surface

- Dip in SLD at Pt/Nafion interface for saturated D_2O indicates hydrophobic surface
- No SLD dip present for PtO → PtO hydrophilic surface

- **As side chain density increases, structure is more complicated**
- **Water concentrations increase near Pt substrate surface (hydrophilic)**
- **Nafion interface and/or water content rearranges with hydrophobic Pt versus hydrophillic Pt surface**

FUEL CELL PERFORMANCE AND DURABILITY

D. L. Wood, J. Chlistunoff, J. Majewski, and R. L. Borup, J. Am. Chem. Soc. 131 (50), 18096-18104 (2009)

Current NR Work

Erik Watkins (LANSCE): Neutron Reflectometry (ASTERIX)
Derek Richard: Neutron Reflectometry, sample prep, and modeling

Substrates

- SiO2
- Pt (on Ti/SiO_2/Si)

Environments

- Dry
- H_2O
- D_2O

Ionomer

- Nafion (~20-30nm dry thickness)

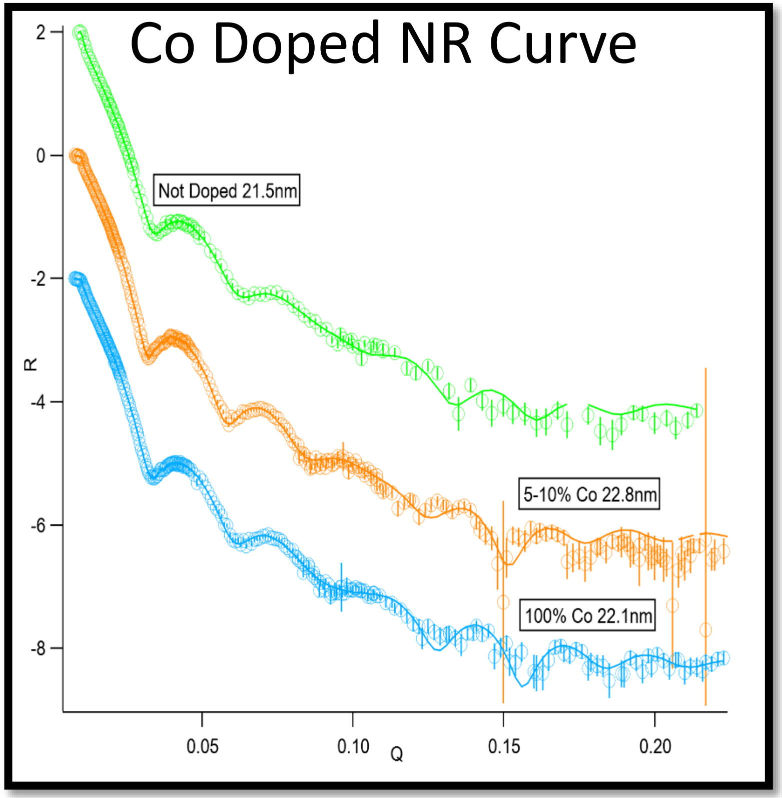
Dopant

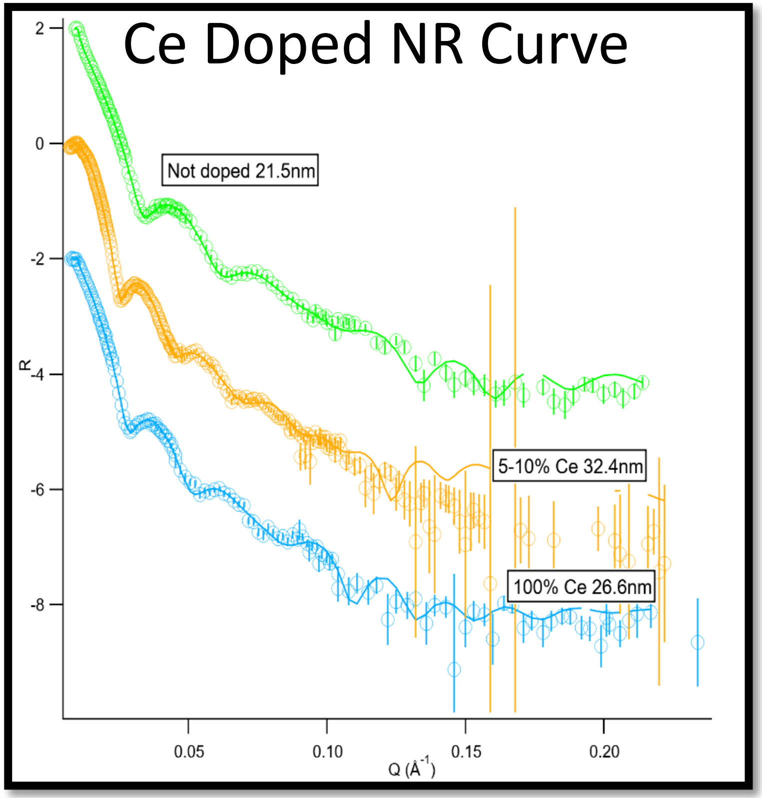
- 5-10% Ce
- 100% Ce
- 5-10% Co
- 100% Co

FUEL CELL PERFORMANCE AND DURABILITY

Effect of Co and Ce Exchange on Structure of Dry Nafion

SiO2/Si Substrate



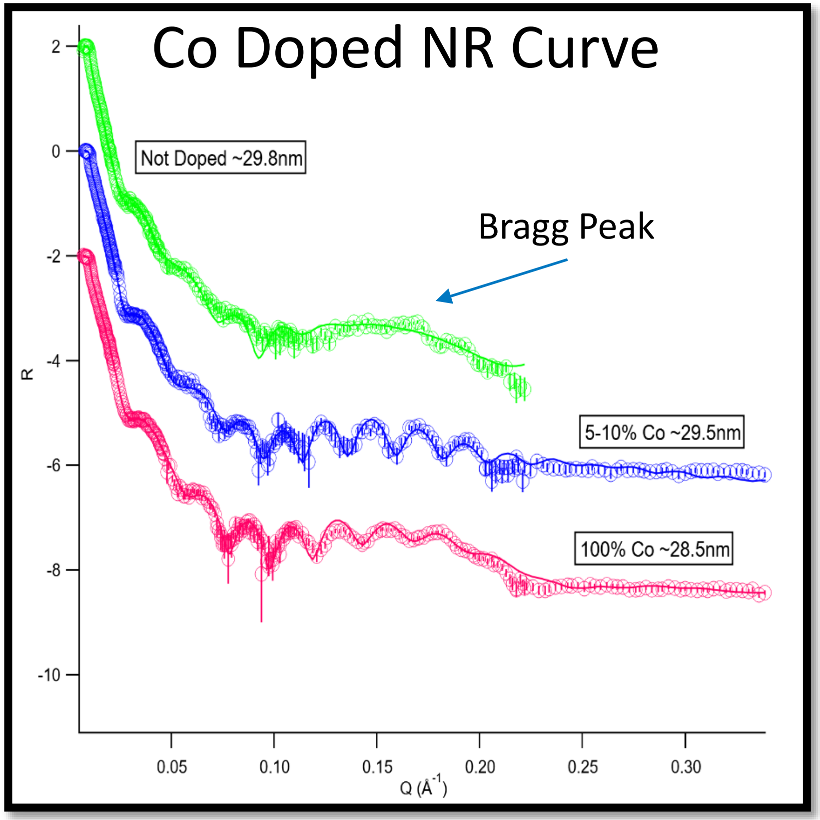


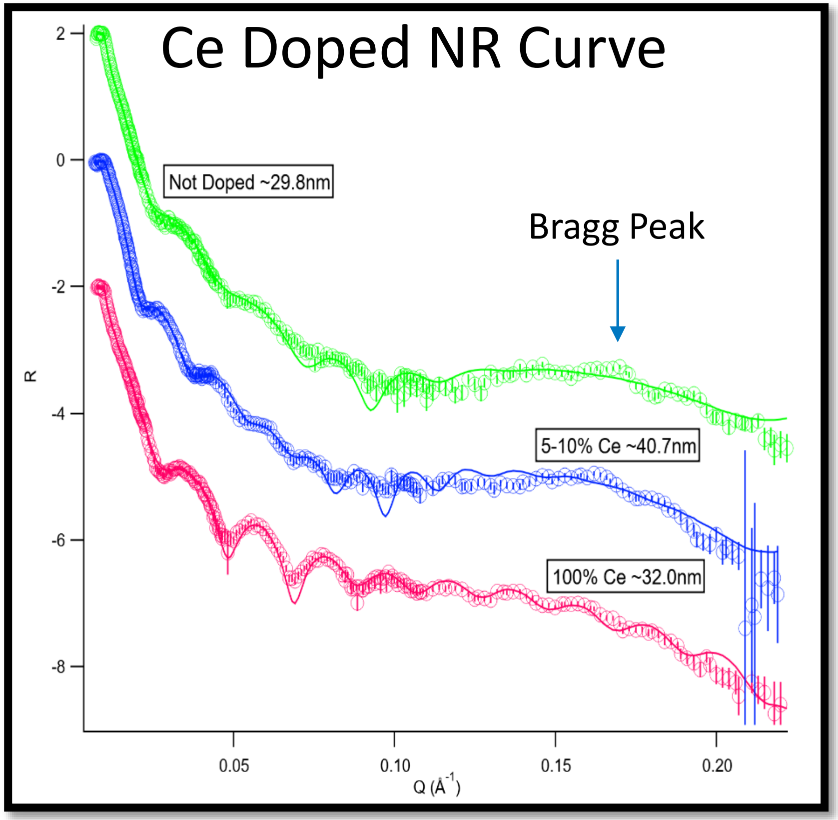
No Bragg peaks on SiO2/Si substrate when dry

- Modeling indicates nearly identical structure
- No obvious layering structure

Effect of Co and Ce Exchange on Structure of Hydrated Nafion

SiO2/Si Substrate





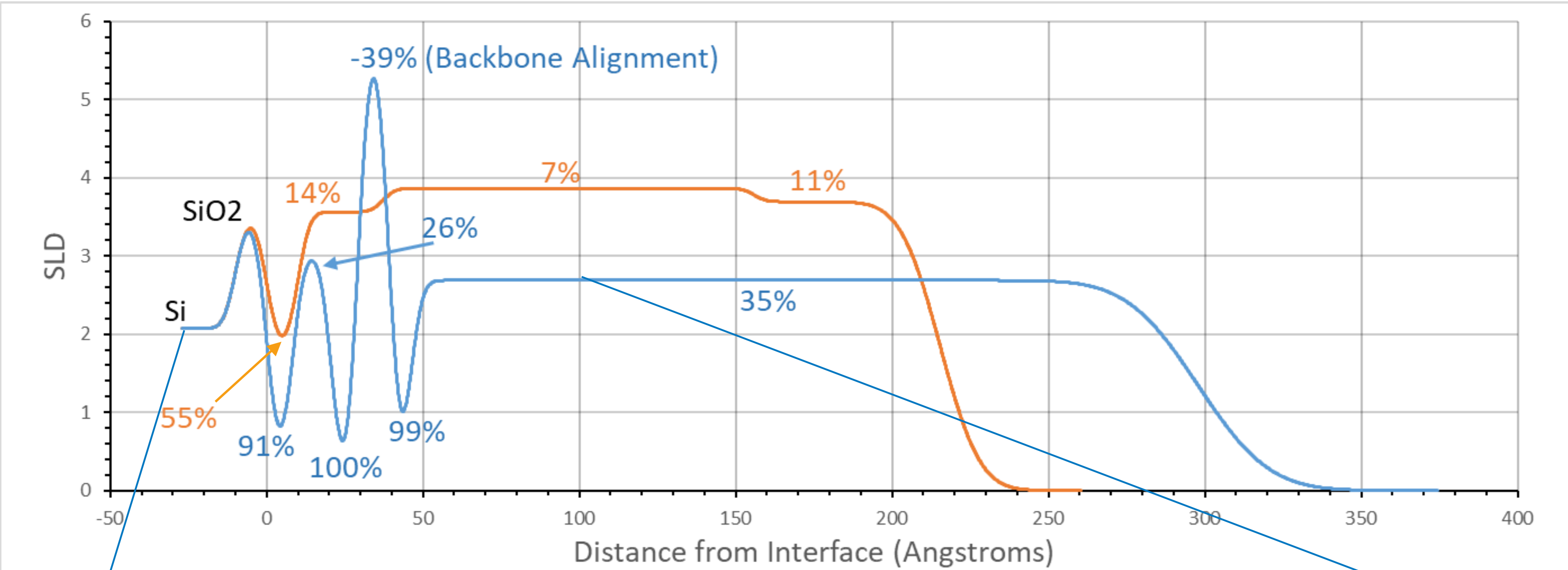
Bragg peak indicates repeated layering structure on SiO_2/Si substrate

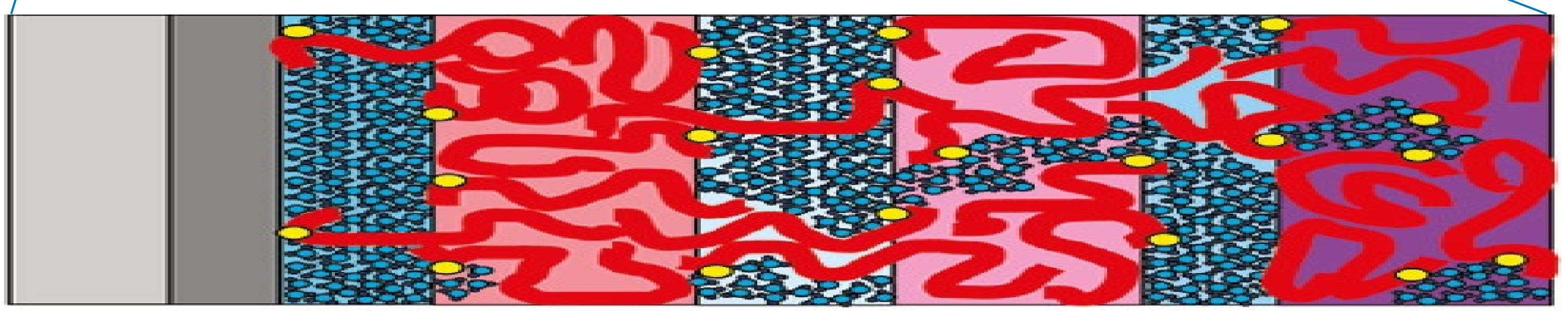
- Consistent with previous studies
- Dopants appear to affect layering structure

- Model: build structure by varying layer thicknesses, and SLD, then back-calculate theoretical curve and minimize variance

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

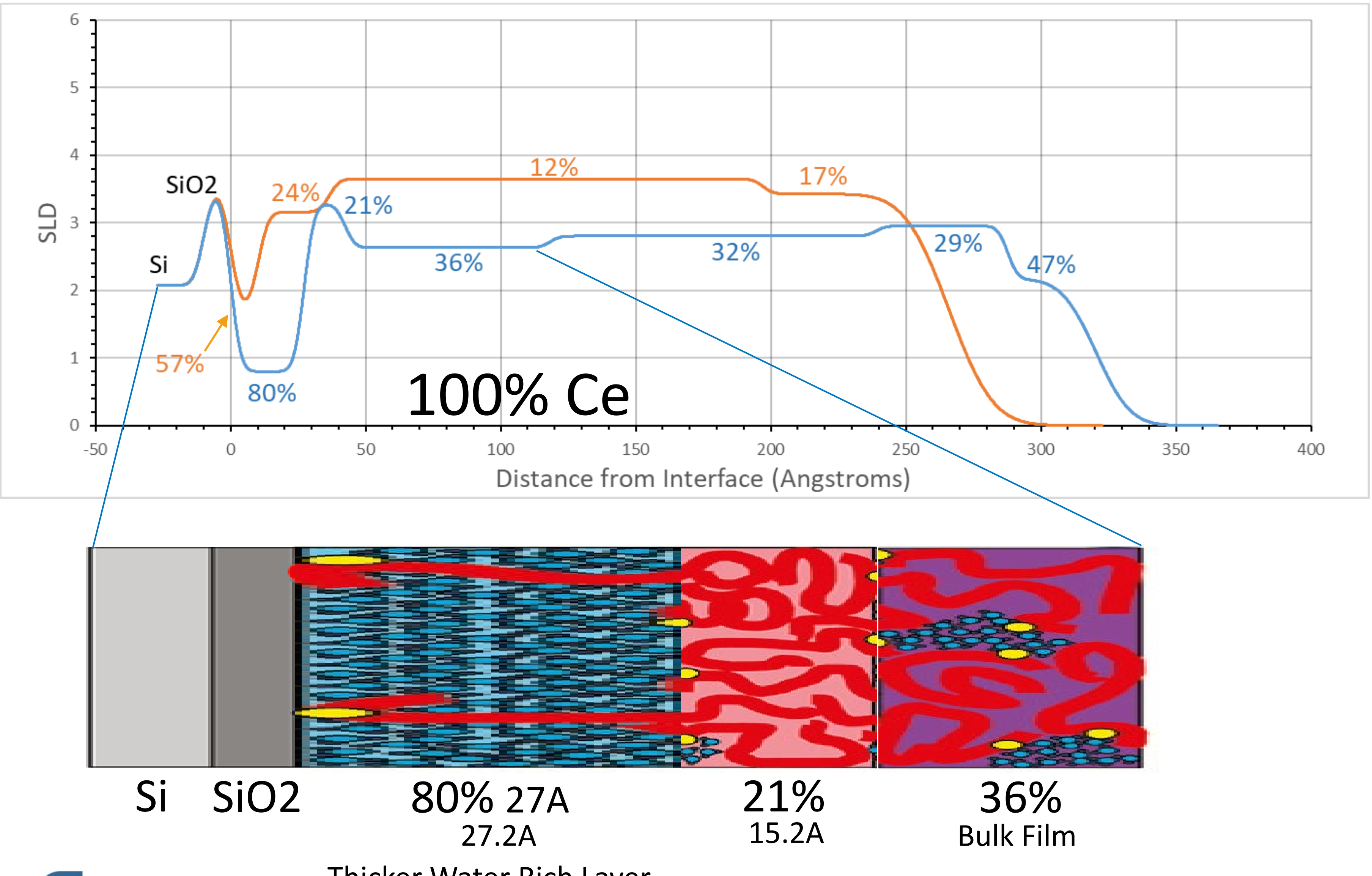
Undoped Film Structure (Hydrated)
8 – layer model





Si	SiO2	91%	26%	100%	-39%	99%	35%
		8.3A	12.5A	8.3A	10.1A Super Dense Region	6.6A	Bulk Film

Doped Film Structure (Hydrated)

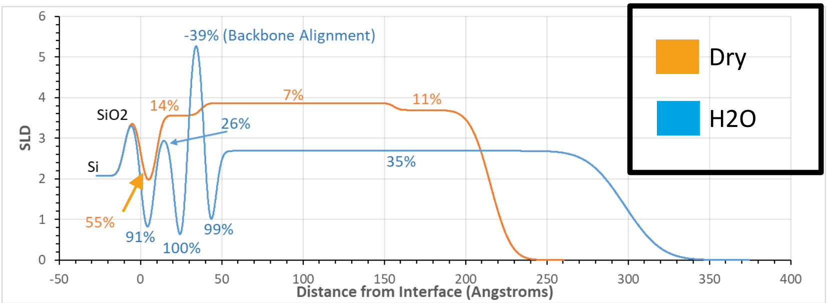


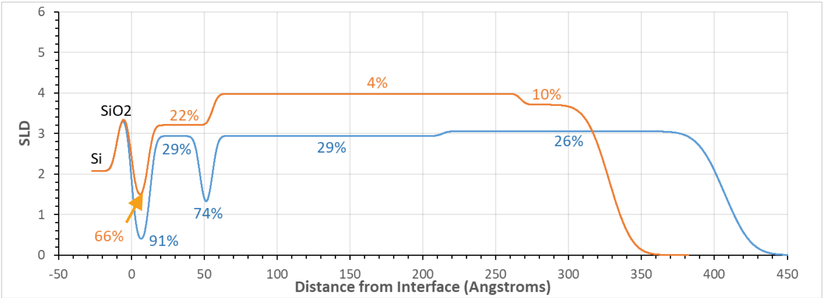
Dura, J.A., et. al, Multilamellar Interface Structures in Nafion, Macromolecules 2009, 42, 4769–4774.

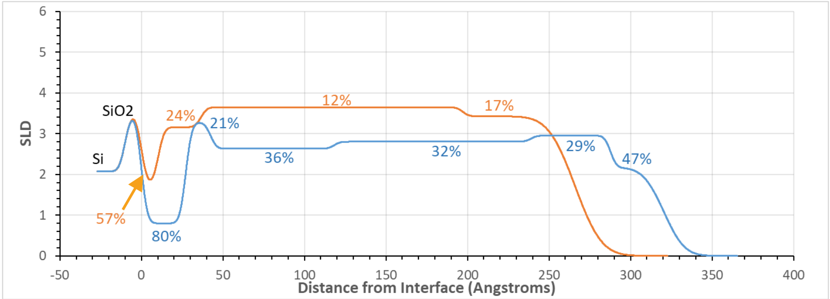
%Water Content by Layer

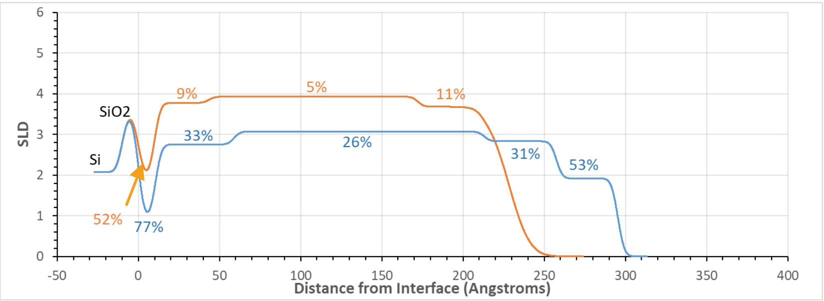
SiO2/Si Substrate

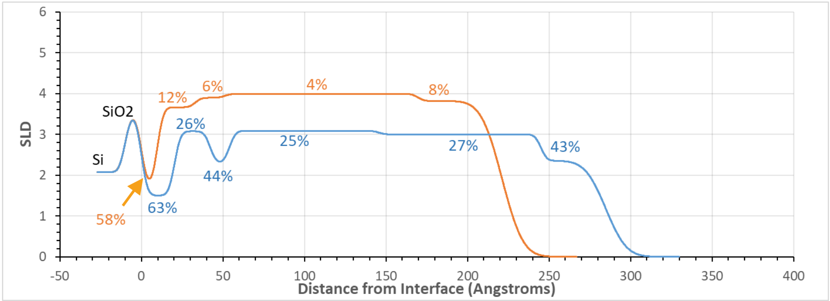
- Nearly identical structure under dry conditions
- Dopants disrupt interface structure observed in undoped films
- Super dense Nafion only observed in undoped film
- 100% exchanged films have larger low SLD layers at interface (higher interface water content)





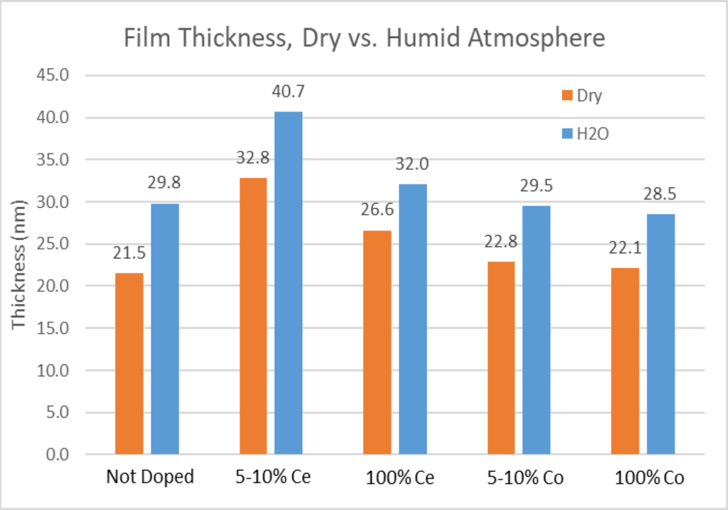


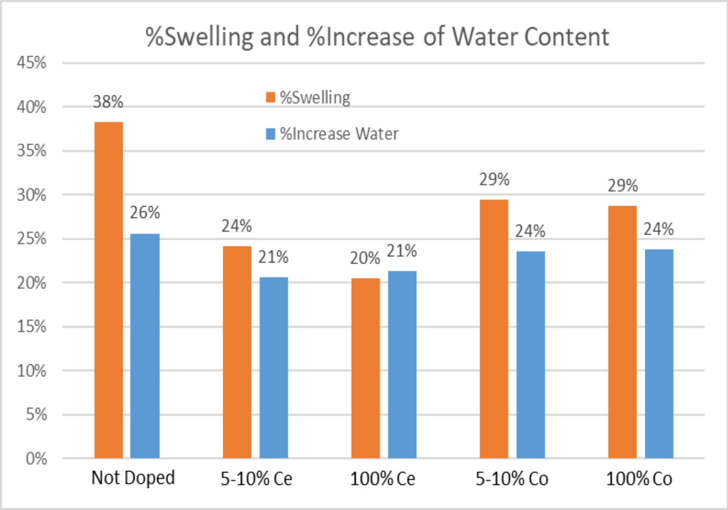


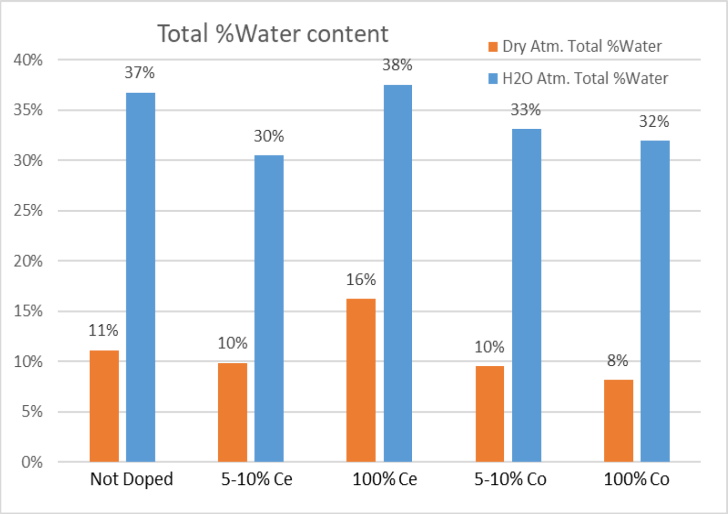


FUEL CELL PERFORMANCE AND DURABILITY

Effect of Dopant on Water Uptake and Swelling



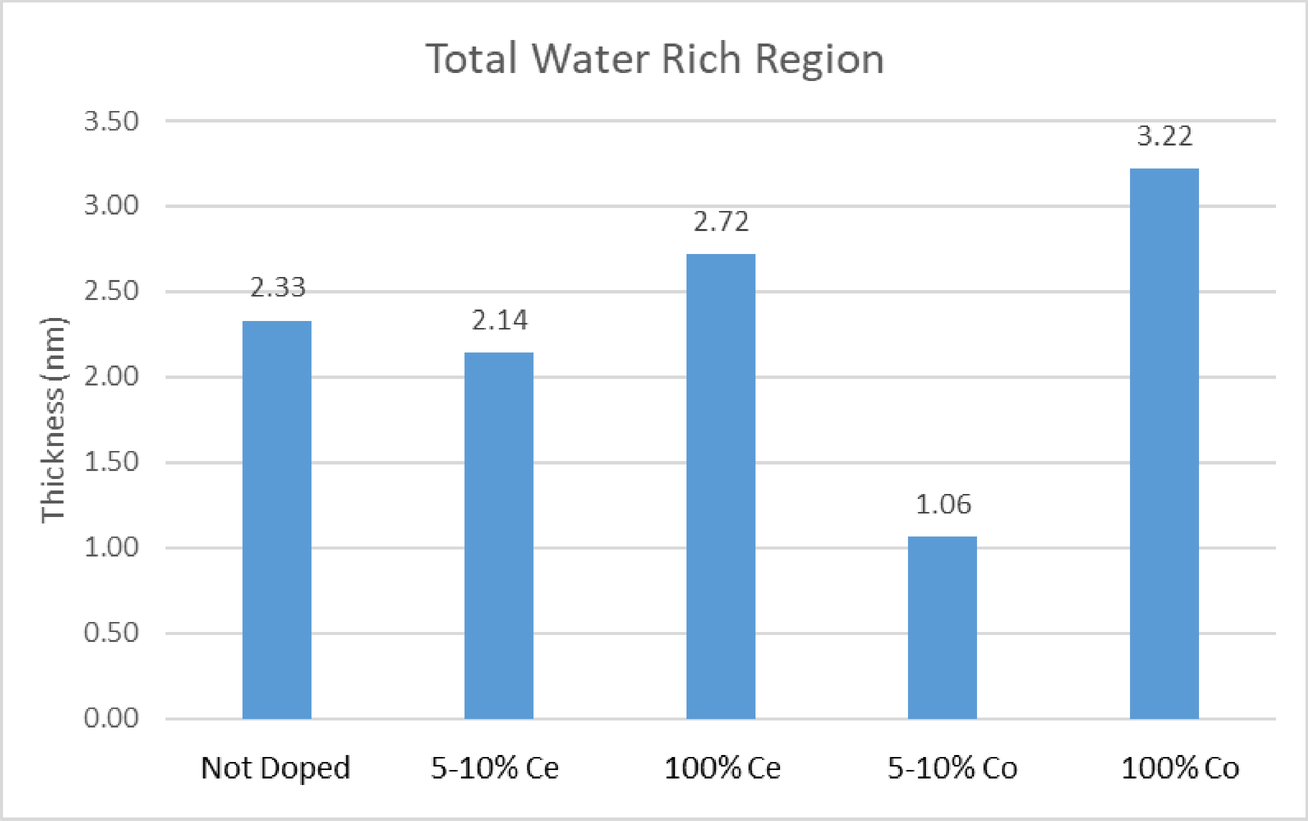




- Doping limits swelling
- Water uptake appears determined by if nafion is doped or not and is not a function of the amount of dopant
- Doping with Ce appears to decrease swelling as conc. Increases
- Ce appears to increase overall water content at high dopant levels and decrease overall water concentration at low dopant levels
- Doping with Co appears to slightly decrease overall water content under all conditions as a function of the amount of dopant

FUEL CELL PERFORMANCE AND DURABILITY

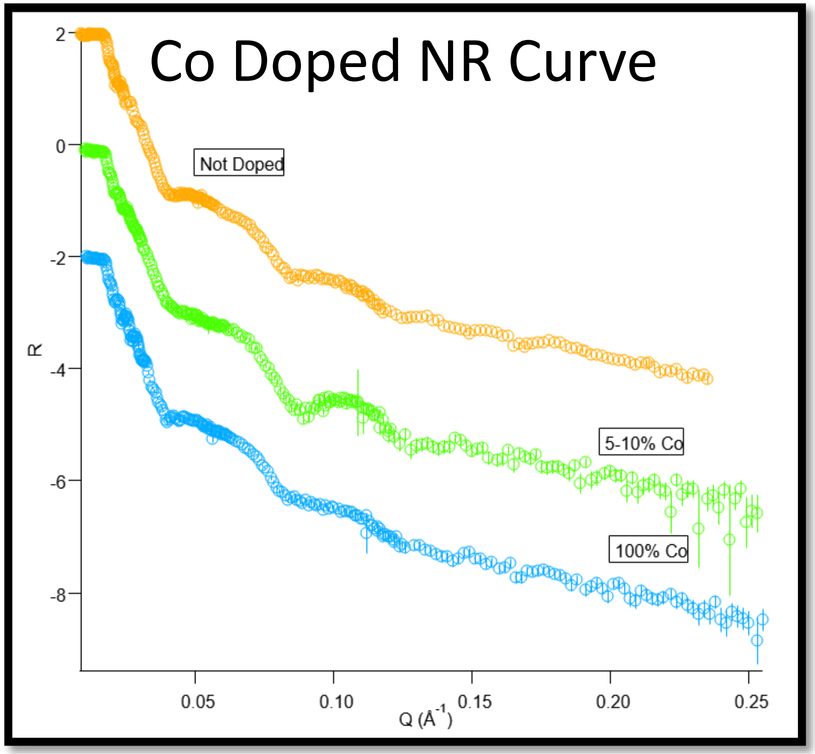
Effect of Dopant on Interface Region

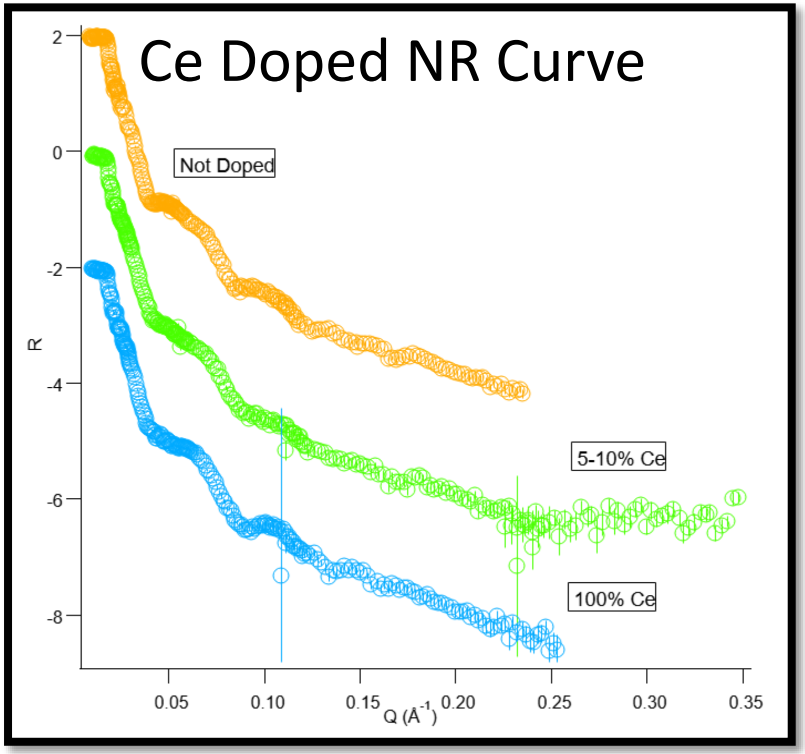


- Water-rich interface region increases at high dopant levels and decreases at low dopant levels

Effect of Co and Ce Exchange on Structure of Hydrated Nafion

Pt Substrate





No obvious Bragg peaks on Pt substrate

- No obvious layering structure
- In-depth modeling needed to determine structural differences
- Preliminary modeling suggests dense Nafion near substrate (consistent)

Summary / Futures

- **Objective:**
  - Use model systems to understand Nafion interactions/structure with Electrocatalysts (Pt/C)
- **Technical Accomplishments:**
  - Model system substrates of Si, Pt/Si and C/Pt
  - Observe structural changes depending upon hydrophobicity of Pt surface (oxidized or metallic Pt)
  - Measurements of membrane swelling with H_2O and D_2O
  - Different ionomer equivalent weights show different swelling
  - Measured thin film ionomer structural changes in ionomer/water structure with cations
  - Cations drastically change Nafion interface structure
    - (Cobalt (leaches out of PtCo/C (alloy) catalysts)
    - (Cerium used for enhanced membrane chemical stability as a radical scavenger)
- **Future Work:**
  - Ionomer variations: Nafion, 3M825, 3M620 (equiv. wts)
  - Additional variables and questions:
    a) Carbon: variations of surface functionalities by partial oxidation
    b) Surface oxidation of Pt by electrochemical potential variation
    c) Ce and Co concentrations
    d) Where is the Dopant in the film?

Supplemental Material

Structure Comparison and Chi Square Values

Sample 3

Layers in r	Dry Chi Sq	H2O Chi S	D2O Chi Sqr	
1	8.04467	19.4282	24.3042	
2	2.76741	6.4345	18.8118	
3	1.73995	6.09444	11.2484	
4	1.20335	3.4367	28.6708	
5	2.20476	1.7907	2.42745	
6	2.4587	2.88709	2.15751	6Layer H2
7				

Dry			
Layer	Thickness	SLD	%H2O content
1	59.339	3.6923	11%
2	118.87	3.8605	7%
3	27.145	3.5611	14%
4	10.05	1.8196	55%
5			
6			
7			
Total thickness =	21.5	nm	
Average % Water =	11%		

H2O			
Layer	Thickness	SLD	%H2O content
1	252.01	2.6862	35%
2	6.6336	-0.01688	99%
3	10.091	5.8055	-39%
4	8.3264	-0.05662	100%
5	12.496	3.0423	26%
6	8.3244	0.34056	91%
7			
Total thickness =	29.8	nm	
Average % Water =	37%		

Sample 4

Layers in r	Dry Chi Sq	H2O Chi S	D2O Chi Sqr	
1	7.35993	34.4084	21.2414	
2	3.6101	4.07062	19.186	
3	3.2427	6.81987	23.6886	
4	1.28418	2.97097	41.3139	
5		2.72192	26.6642	
6		2.08561		6.1 H2O
7				

Dry			
Layer	Thickness	SLD	%H2O content
1	68.783	3.4245	17%
2	160.69	3.6455	12%
3	26.164	3.1564	24%
4	10.353	1.7331	57%
5			
6			
7			
Total thickness =	26.6	nm	
Average % Water =	16%		

H2O			
Layer	Thickness	SLD	%H2O content
1	32.674	2.1665	47%
2	48.896	2.9503	29%
3	120.66	2.8011	32%
4	75.816	2.6299	36%
5	15.169	3.2762	21%
6	27.215	0.79703	80%
7			
Total thickness =	32.0	nm	
Average % Water =	38%		

Sample 9

Layers in r	Dry Chi Sq	H2O Chi S	D2O Chi Sqr	
1	15.2673	34.1862	12.6037	
2	5.68895	12.8675	3.95165	
3	3.5612	9.21055	9.05647	
4	1.9766	7.61511	7.72644	
5	2.72775	2.91715	4.1263	D2O Matc
6	4.92927	4.55861	2.04861	
7		4.07219		

Dry			
Layer	Thickness	SLD	%H2O content
1	60.412	3.7098	10%
2	211.59	3.9796	4%
3	44.099	3.2046	22%
4	11.585	1.395	66%
5			
6			
7			
Total thickness =	32.8	nm	
Average % Water =	10%		

H2O			
Layer	Thickness	SLD	%H2O content
1	193.49	3.0509	26%
2	157.89	2.9389	29%
3	8.4236	1.0219	74%
4	34.11	2.9347	29%
5	13.017	0.31422	91%
6			
7			
Total thickness =	40.7	nm	
Average % Water =	30%		

Sample 12

Layers in r	Dry Chi Sq	H2O Chi S	D2O Chi Sqr	
1	6.09846	43.7968	6.05808	
2	2.35424	7.28234	4.58479	
3	2.59696	4.37151	4.69145	
4	1.61799	2.66648	3.55537	
5	1.73386	2.49636	3.5841	
6	0.83004	1.7279	4.2918	thin top la
7				

Dry			
Layer	Thickness	SLD	%H2O content
1	51.583	3.8175	8%
2	118.56	3.9905	4%
3	18.124	3.8957	6%
4	23.167	3.6618	12%
5	9.812	1.7204	58%
6			
7			
Total thickness =	22.1	nm	
Average % Water =	8%		

H2O			
Layer	Thickness	SLD	%H2O content
1	39.83	2.353	43%
2	99.285	2.9982	27%
3	91.737	3.0845	25%
4	11.859	2.2944	44%
5	21.84	3.0755	26%
6	20.324	1.5	63%
7			
Total thickness =	28.5	nm	
Average % Water =	32%		

Sample 13

Layers in r	Dry Chi Sq	H2O Chi S	D2O Chi Sqr
1	8.15635	11.3123	10.0111
2	4.03816	26.8603	26.231
3	1.53957	8.50793	9.95548
4	1.70491	3.57004	7.54793
5	1.1751	2.0749	2.03435
6			
7			

Dry			
Layer	Thickness	SLD	%H2O content
1	17.015	3.5391	15%
2	38.863	3.6794	11%
3	128.92	3.9274	5%
4	33.366	3.7739	9%
5	10.048	1.9625	52%
6			
7			
Total thickness =	22.8	nm	
Average % Water =	10%		

H2O			
Layer	Thickness	SLD	%H2O content
1	37.847	1.9173	53%
2	44.438	2.8307	31%
3	154.19	3.0678	26%
4	48.299	2.752	33%
5	10.634	0.92838	77%
6			
7			
Total thickness =	29.5	nm	
Average % Water =	33%		

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Modeling of Ionomer Films

- Software: MOTOFIT.
- Create model consisting of multiple layers
- Each layer has three variables: thickness, roughness at the interface, and SLD (scattering length density)
- SLD contains information about chemical composition.
- Model calculates the reflectivity of a sample with that structure, calculates a chi square of the fit, and continues that iteration until a minimum in the chi squared is found.
- Best-fit reflectivity curve and the SLD profile that generates that curve.
- SLD profile is a function of depth into the sample.

- *Use of multiple layers used to find further structure in the water distributions within the polymer layer.*
  - Adjust the slds in other locations.
  - Surface roughness between these layers can be extremely high and yield a distribution that looks almost linear across the film, or the roughness may be more narrow in preference of more distinct regions.

Comments

- We repeated the measurements of the 3M polymers on Pt in dry conditions and confirmed the non-uniform polymer distribution in the film (less density at the air interface). That complicates things substantially for those 2 cases, especially trying to be quantitative about the water distribution after swelling.

- Mixed H_2O and D_2O in ratio for SLD variance to be = zero. Exposed to vapor, to look at polymer distribution with no net change from water. Showed same distribution as H_2O.

- Exacting water concentrations/gradient in the films

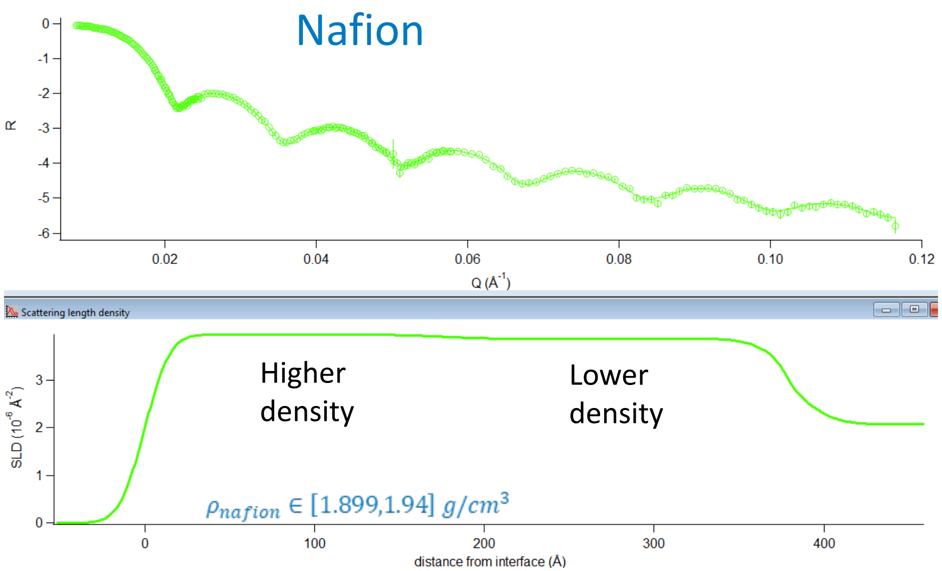
- The samples equilibrate for about an hour. Samples remain in controlled atmosphere during neutron reflectometry. The data are usually taken somewhere between 12 and 24 hours per sample. The modelling time varies, but ~ 2-3 hours per dataset

Ionomer Swelling and SLD for Nafion, 3M825, 3M620

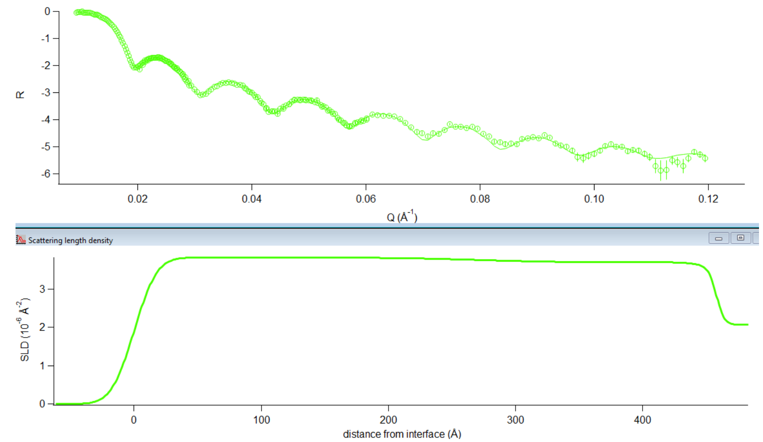
		Thickness	SLD	% Swelling	% Volume Fraction D2O
Nafion on Si (Dry)	Dry	366	3.89		
Nafion on Si (Wet)	Wet	434	4.74	19%	35%
Nafion on Pt (Dry)	Dry	407	4.19		
Nafion on Pt (Wet)	Wet	496	4.84	22%	31%
3M825 on Si (Dry)	Dry	440	3.79		
3M825 on Si (Wet)	Wet	542	4.84	23%	42%
3M825 on Pt (Dry)	Dry	464	3.98		
3M825 on Pt (Wet)	Wet	553	5.16	19%	51%
3M620 on Si (Dry)	Dry	318	3.3		
3M620 on Si (Wet)	Wet	620	5.11	95%	60%
3M620 on Pt (Dry)	Dry	353	3.44		
3M620 on Pt (Wet)	Wet	559	5.18	58%	61%

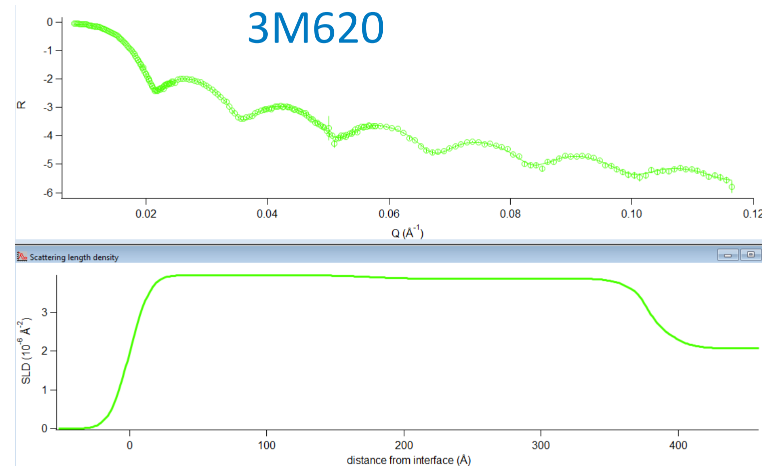
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Dry Ionomer Films on Si Substrates



3M825

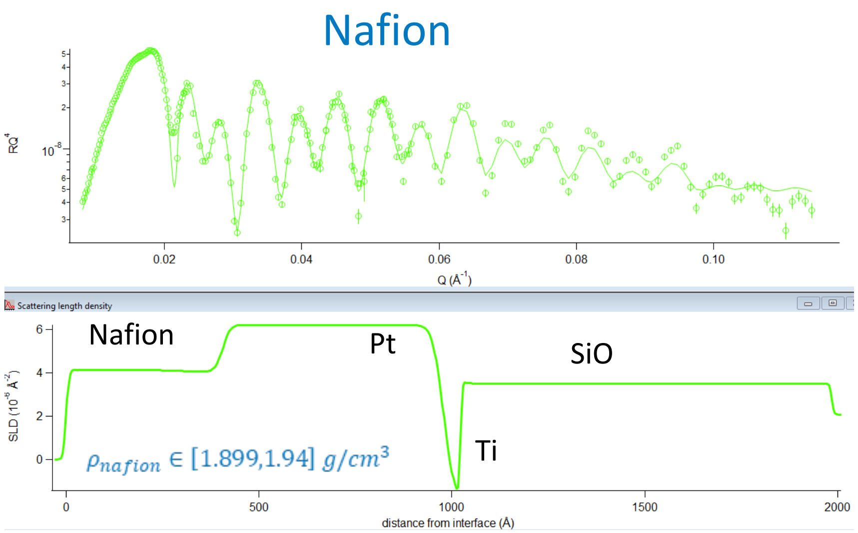


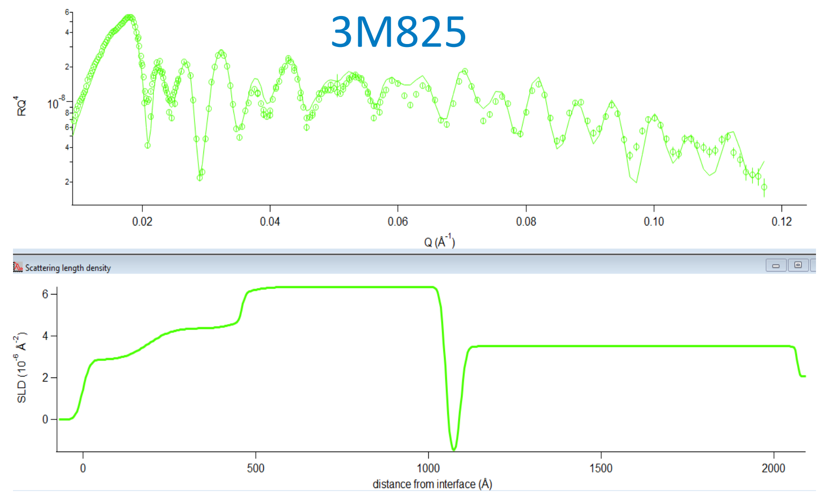


- All ionomers slightly decrease in density toward substrate
- Similar feature for Nafion on Pt

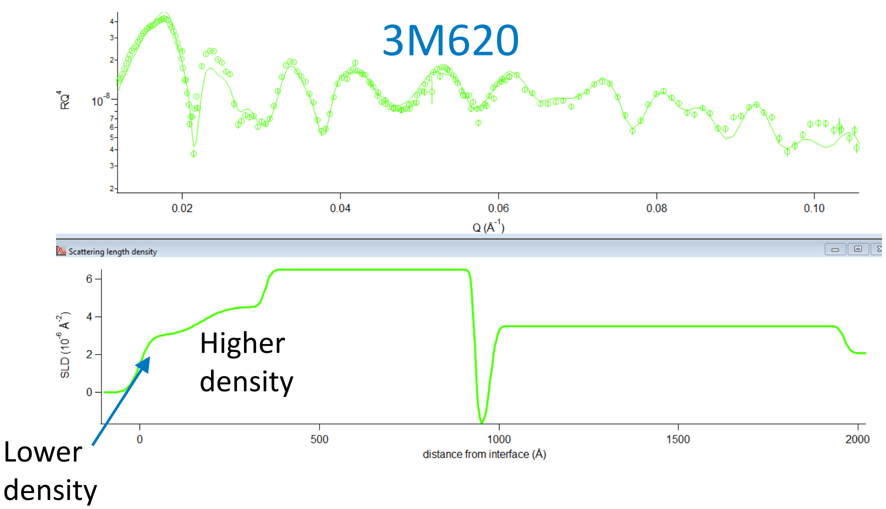
FUEL CELL PERFORMANCE AND DURABILITY

Dry Ionomer Films on Pt Substrates





- Nafion decreases in density toward Pt substrate.
- 3M ionomers increase in density toward Pt substrate (repeated)

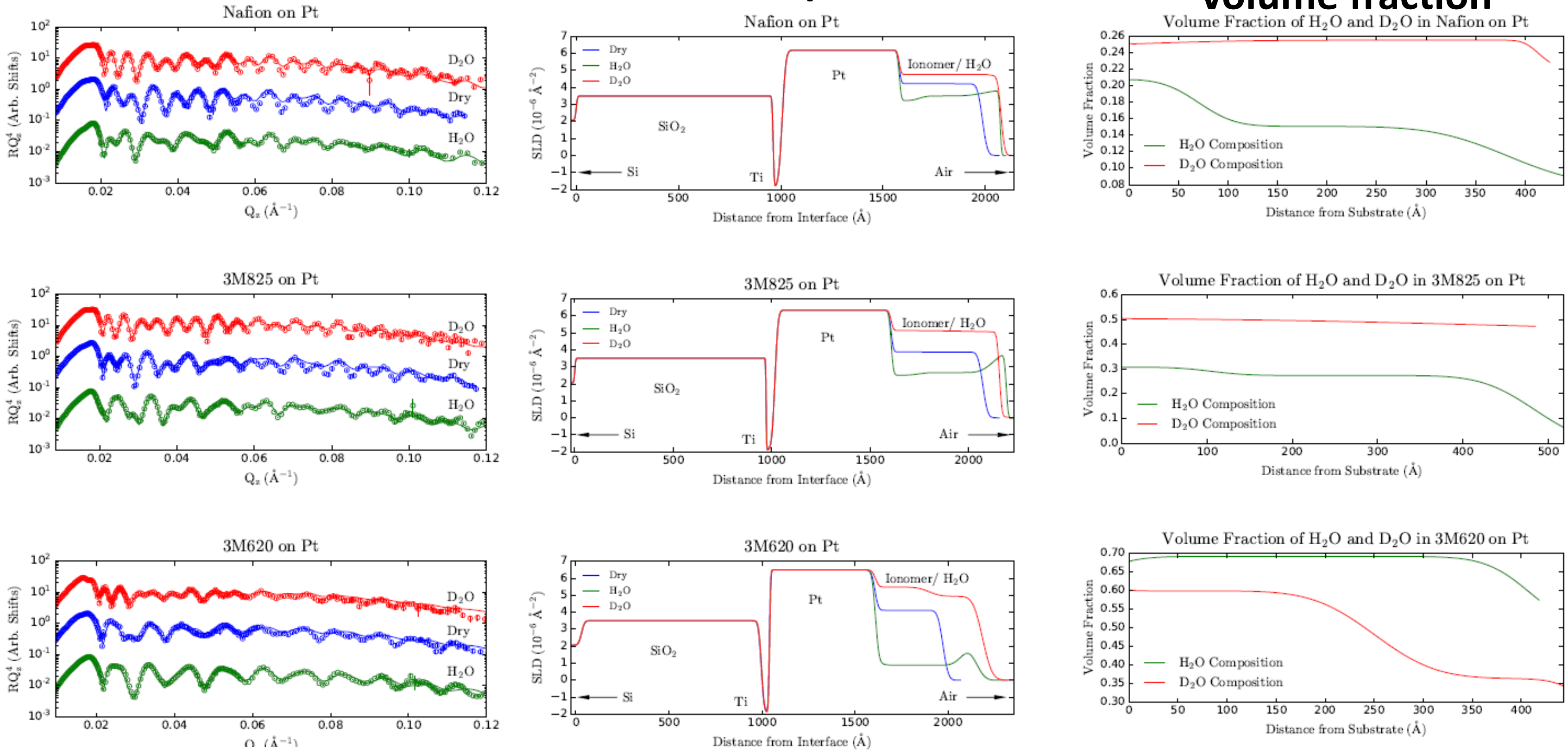


FUEL CELL PERFORMANCE AND DURABILITY

Combined H_2O and D_2O for zero SLD

Nafion, 3M825, 3M620 Ionomers

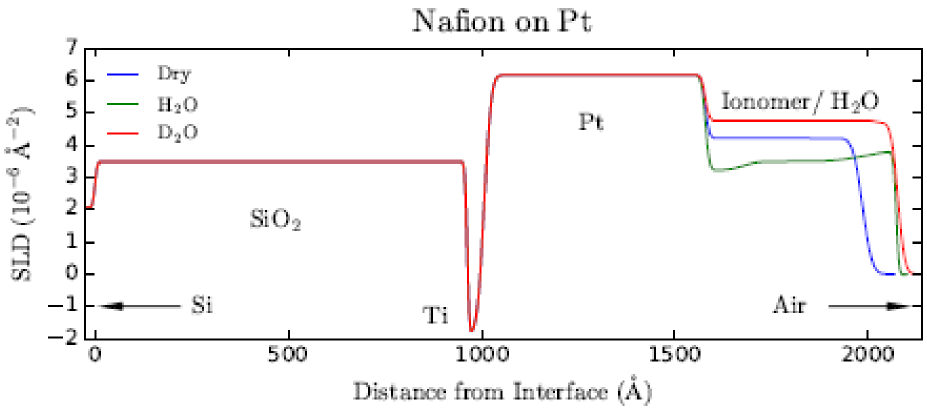
Reflectivities | **Fitted SLD profiles** | **Calculated water volume fraction**

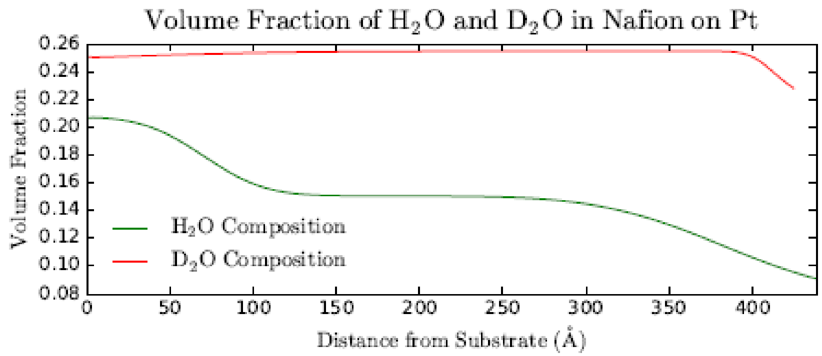


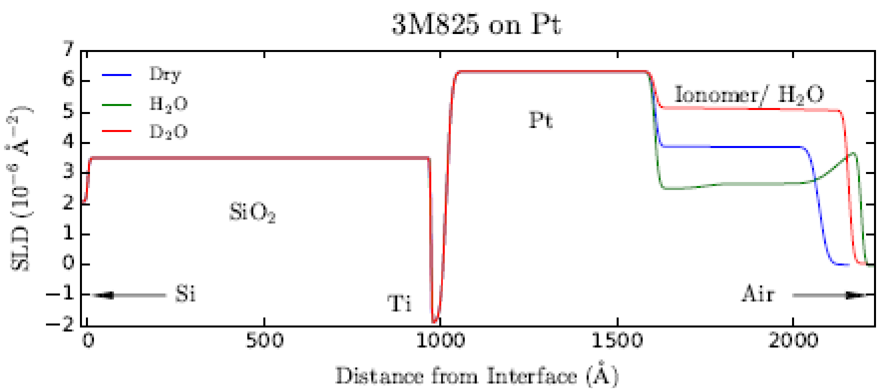
Fits show good agreement demonstrating water concentrations are higher near the surface of the Pt substrate

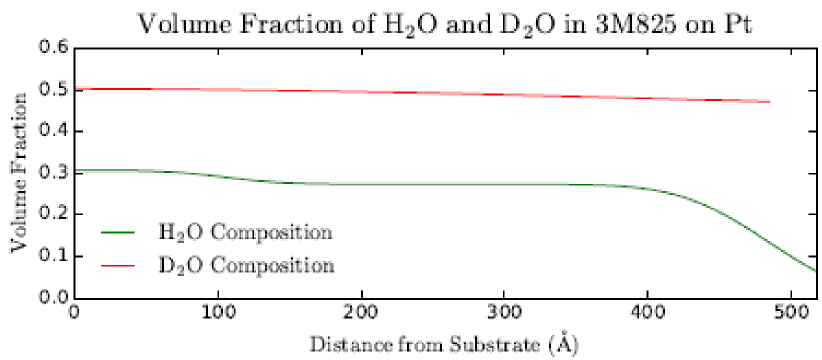
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

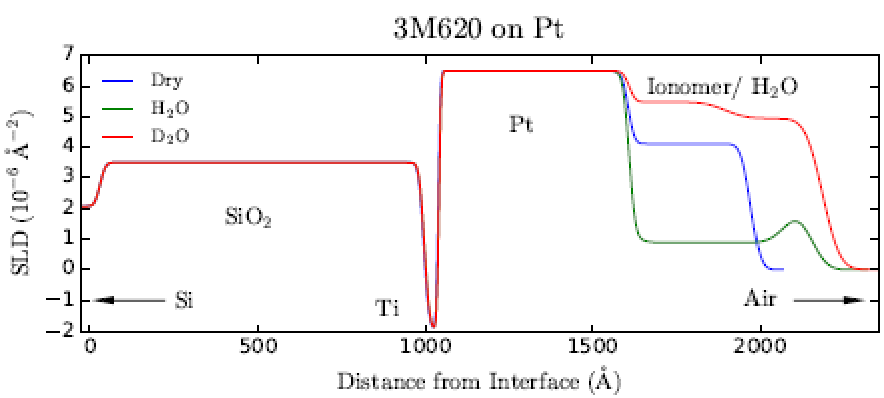
Fitted SLD profiles
Combined H_2O and D_2O for zero SLD

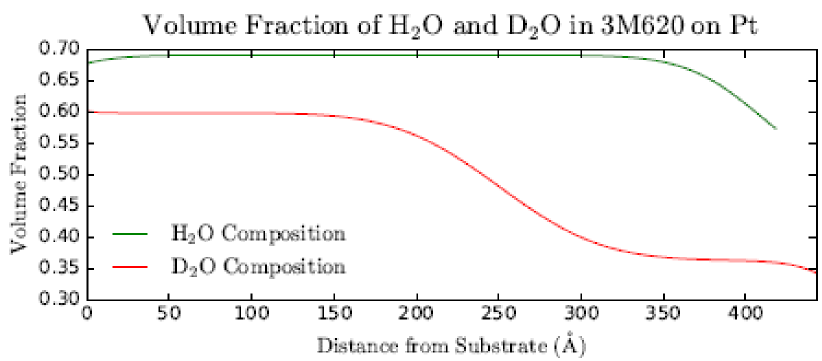






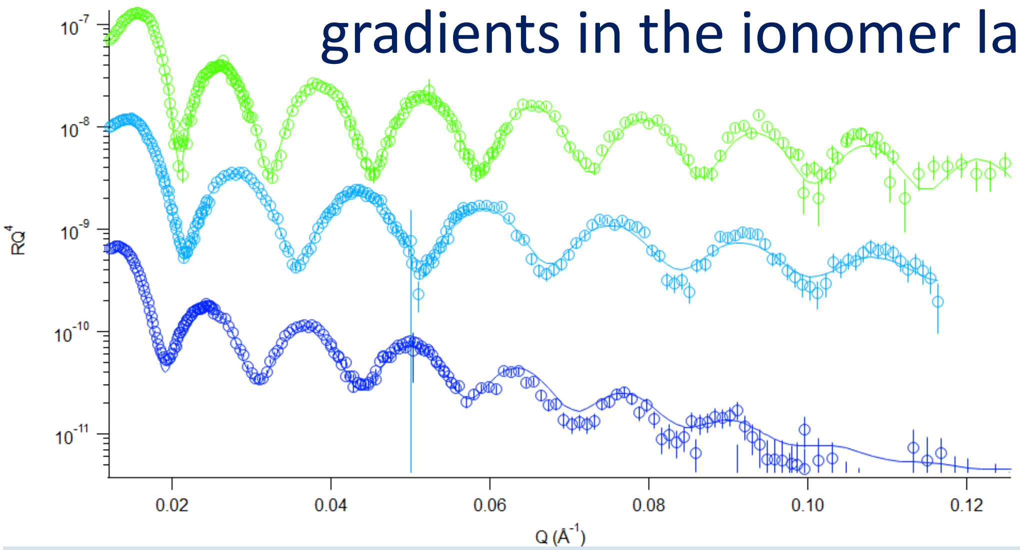




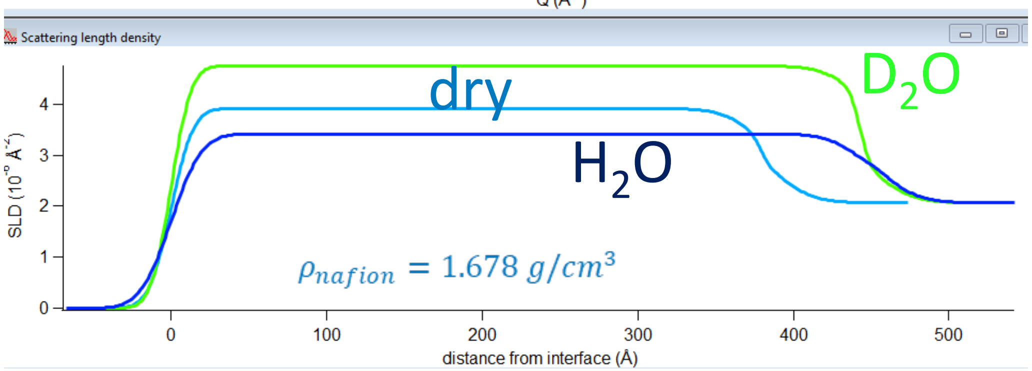


NR of Nafion on Si, Dry and Wet (H_2O and D_2O)

2 Layer Model. Does not account for concentration gradients in the ionomer layers. (2 Layers = Si, Nafion)



Good Fit



D_2O: 16.9% Swell

$x_{D2O} = 33.7\%$

H_2O: 18.1% Swell

$x_{H2O} = 11.1\%$

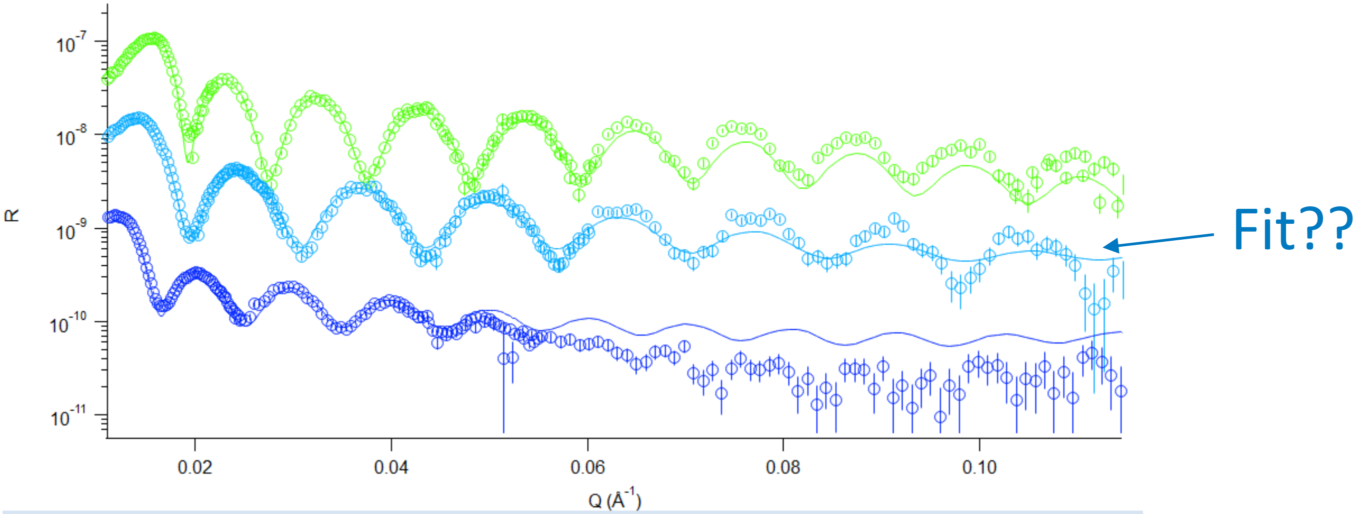
Note:

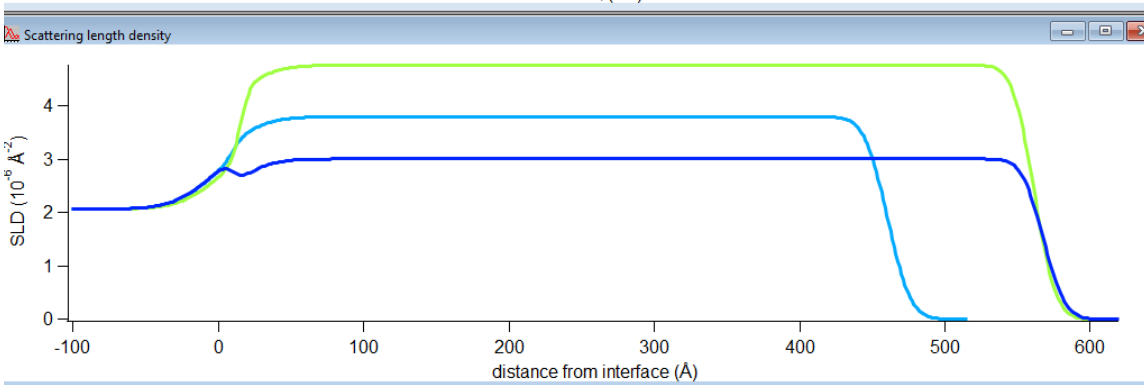
D_2O positive coherent scattering length

H_2O negative coherent scattering length

3M825

High Q fits are not good. Need more layers.



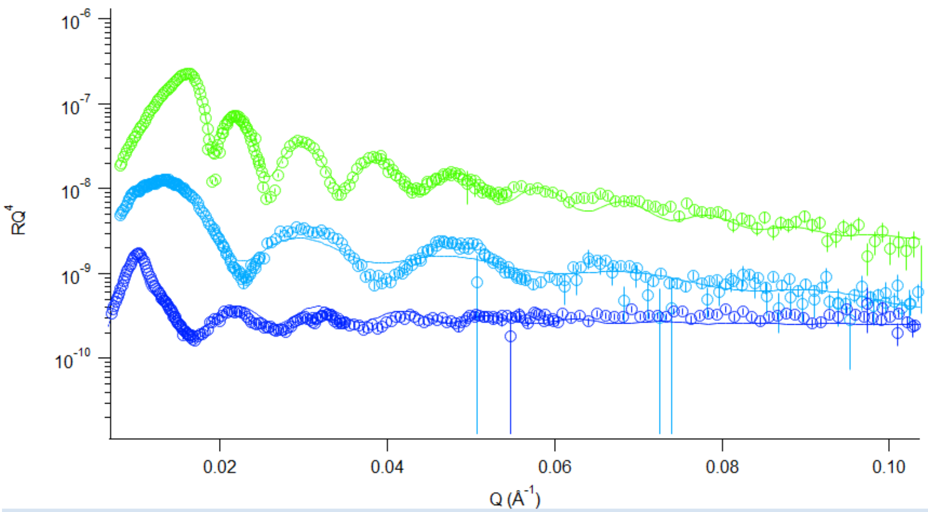


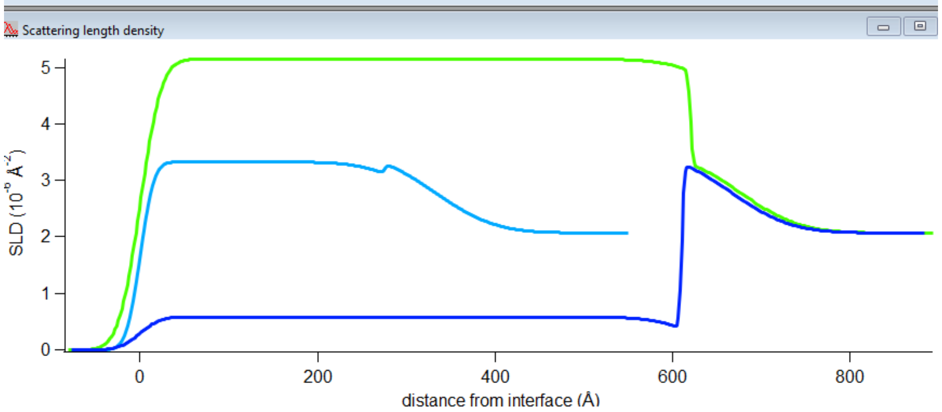
D_2O: 21.3% Swell
x_{D2O} = 37.4%
H_2O: 23.9% Swell
x_{H2O} = 18.1%

As side chain density increases, structure is more complicated

3M620

High Q fits are not good. Need more layers.



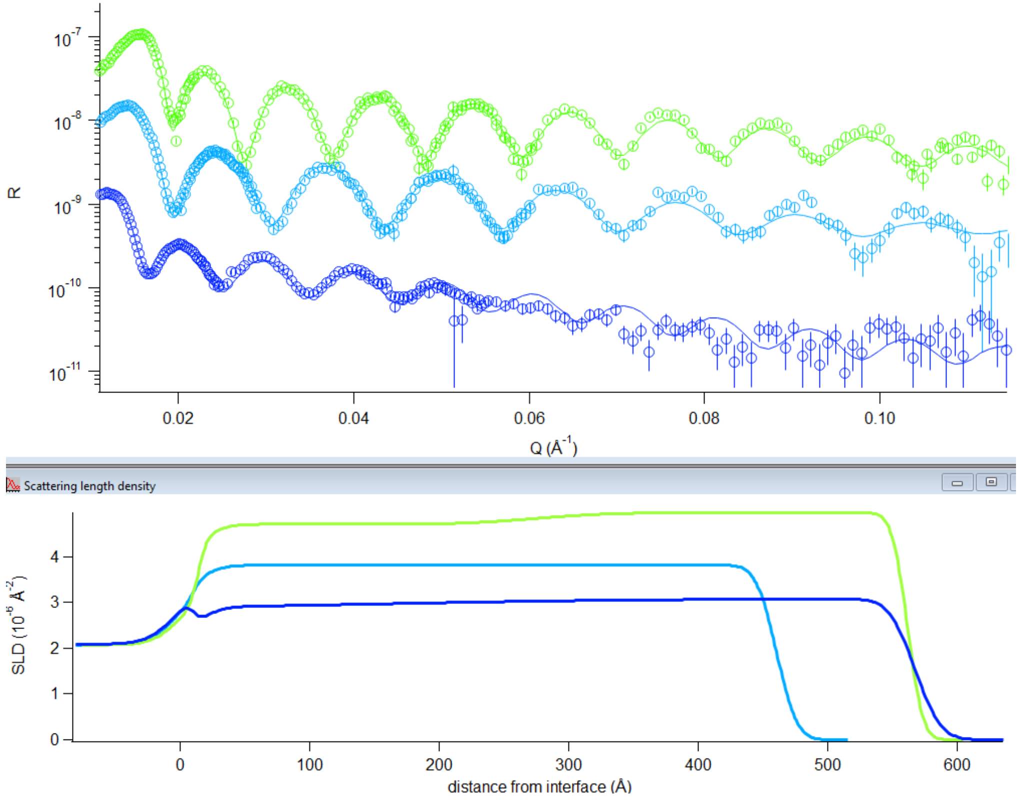


As side chain density increases, structure is more complicated

FUEL CELL PERFORMANCE AND DURABILITY

3M825/Si – 3 Layer Model

3 Layer Model. Add extra layer to ionomer to see concentration gradients. (3 Layers – Si, 2 layers of ionomer)

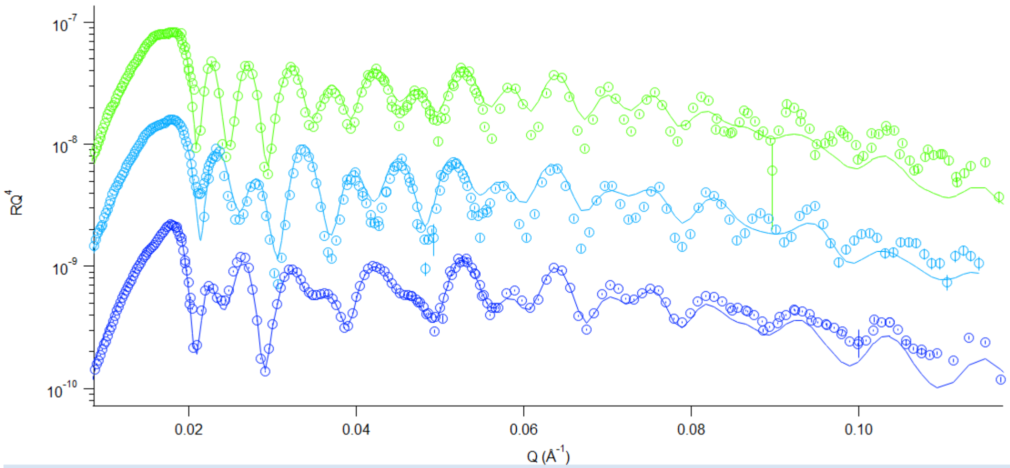


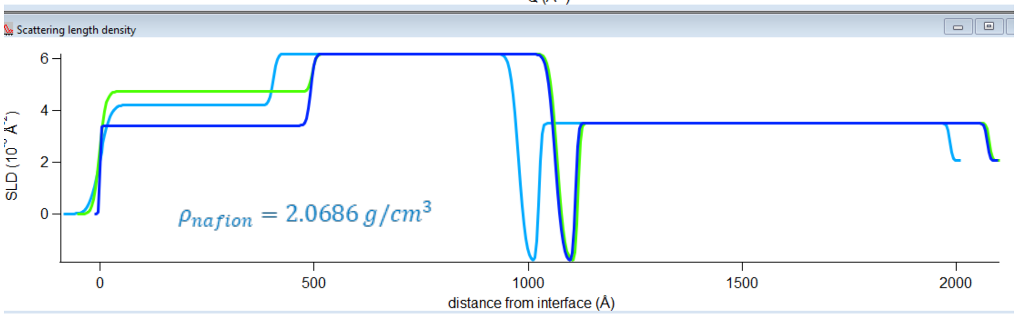
Much better fit with 3-layer model
(2 ionomer layers)

→ 3M ionomers have more complicated structure than does Nafion

Nafion/Pt/Ti/Si – 4 Layer Model

(1 ionomer Layer)





Model captures major features, but high Q loses structure. Needs more layers

D_2O: 22.4% Swell

x_{D2O} = 24.0%

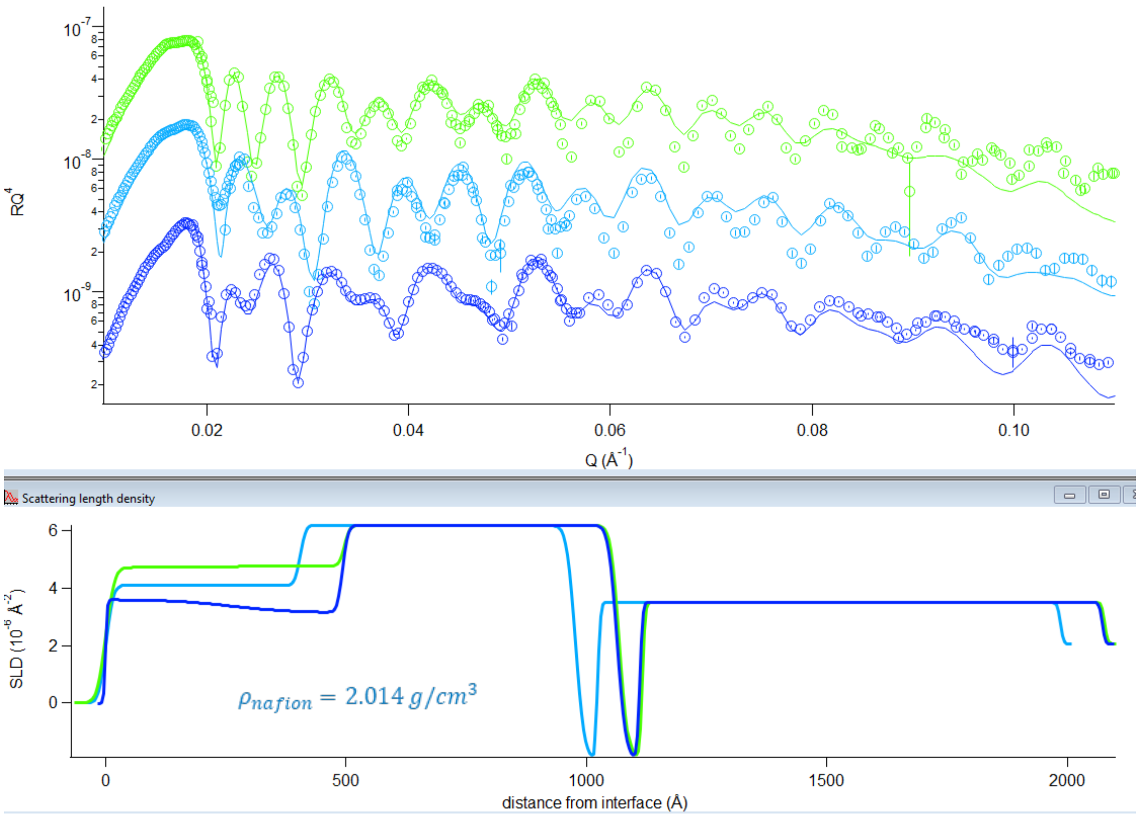
H_2O: 21.3% Swell

x_{H2O} = 20.0%

Nafion has simple structure on Si, but more complicated structure on Pt

FUEL CELL PERFORMANCE AND DURABILITY

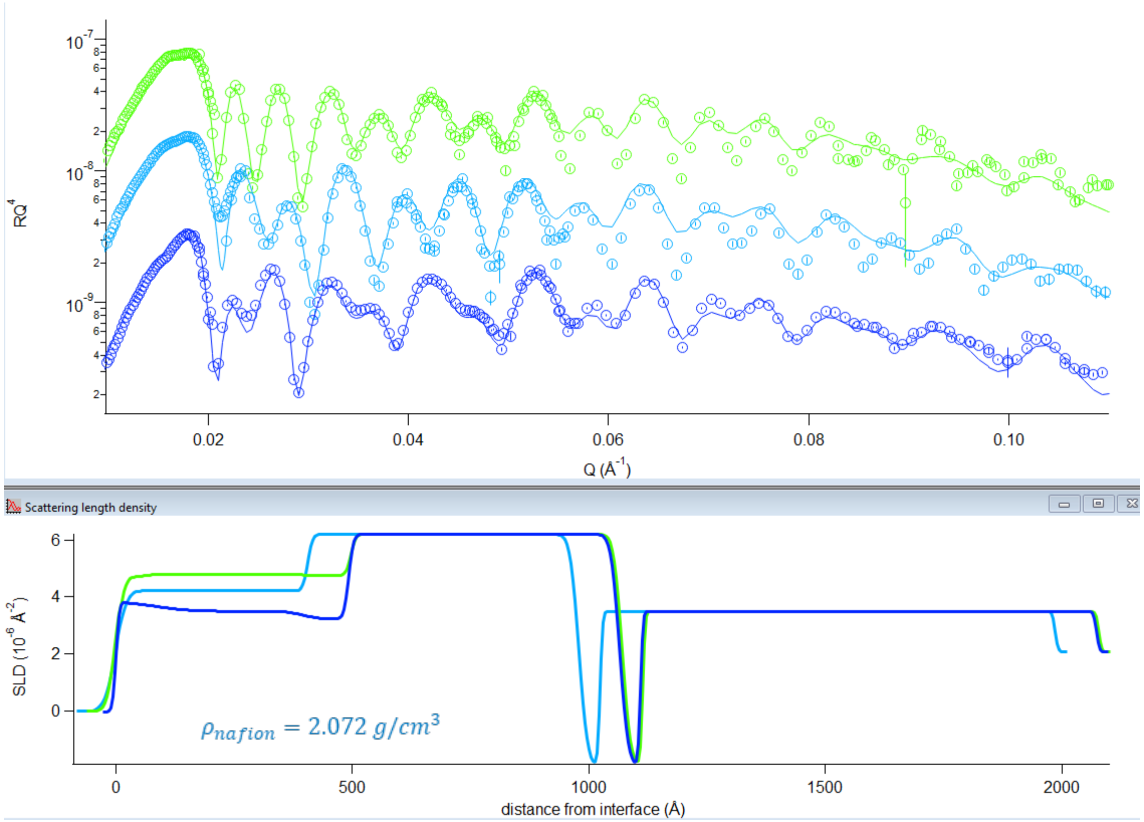
Nafion/Pt/Ti/Si – 5 Layer Model



2 ionomer layer model captures major features, but high Q loses structure. Still needs more layers

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Nafion/Pt/Ti/Si – 6 Layer Model



3-ionomer layer model shows high Q structure now present in fit when water concentration increases near Pt surface.

Nafion requires 3 ionomer layers to adequately describe structure on Pt